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DEVELOPMENT OF REGENERABLE FIBERS FOR REMOVAL OF SULFUR DIOXIDE FROM WASTE GASES

by
R. W. Fuest
M. P. Harvey
C. W. Lee
S. A. Black

July 1970

FINAL REPORT

Contract No. PH 86-68-74

Prepared For

National Air Pollution Control Administration
Department of Health, Education & Welfare

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UNIROYAL, INC.
Research Center
Wayne, New Jersey 07470

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FOREWORD

This is the final report on the work performed by UNIROYAL, INC. under Contract No. PH 86-68-74 during the period July 1, 1968 to August 26, 1969. The first phase of the work (January 1 to June 30, 1968) was described in a previous technical report, dated November 1968 (PB No. 185-093).

The work was conducted at the Uniroyal Research Center in Wayne, New Jersey under the administrative direction of Dr. J. S. Lasky and later Dr. R. L. Bergen, Jr. Dr. R. W. Fuest served as Principal Investigator.

Mr. E. D. Margolin, National Air Pollution Control Administration, 5710 Wooster Pike, Cincinnati, Ohio 45227, served as Project Officer.

ABSTRACT

Fibers comprised of a blend of resin and a polymer which contains basic nitrogen groups were prepared and evaluated as sorbents for removing SO_2 from waste gases. The effect of such variables as temperature, moisture, loading of sorbent, fiber denier, and SO_2 concentration in the gas stream were studied. The chemistry and mechanism of the sorption and regeneration processes were elucidated. Preliminary economic and engineering analyses were performed.

SUMMARY

The rate and capacity of SO_2 sorption from SO_2-N_2 mixtures and from simulated flue gas mixtures by sorbent-loaded fibers were determined as a function of such variables as temperature, loading of sorbent in fiber, hydrophilicity, humidity in gas stream, fiber denier, and draw ratio of fiber. The effect of repeated sorption-regeneration cycling upon physical and sorptive properties of the fibers was studied and the maximum temperature to which fibers could be exposed was determined.

It was found that the greatest influence upon rate and capacity was the loading of sorbent polymer in the fiber. A significant technical achievement was the preparation of polypropylene-SSQ (styrene-dimethylaminopropyl maleimide copolymer) fiber containing 60% SSQ which had sufficient physical strength to allow fabrication into any desired type of assembly (felts, knits, woven fabrics etc.). The effects of drawing the fiber, addition of hydrophilic material, and fiber denier were of much smaller magnitude.

Regeneration studies were performed on the more promising fibers by carrying them through multiple cycles of sorption and regeneration. Thermal methods for regeneration (involving the use of inert gas, steam or vacuum) were investigated. An important finding was that oxidation of some of the SO_2 to sulfate occurs during the sorption process, constituting an undesirable side reaction which is not reversible under normal regeneration conditions. Factors influencing the formation of sulfate and methods for restoration of the original sorptive capacity of the fiber were investigated. It was found that the sulfate could be removed from the fiber by treatment with aqueous base solutions.

Preliminary economic analysis of the process showed that a long service life was a necessity for economic feasibility.

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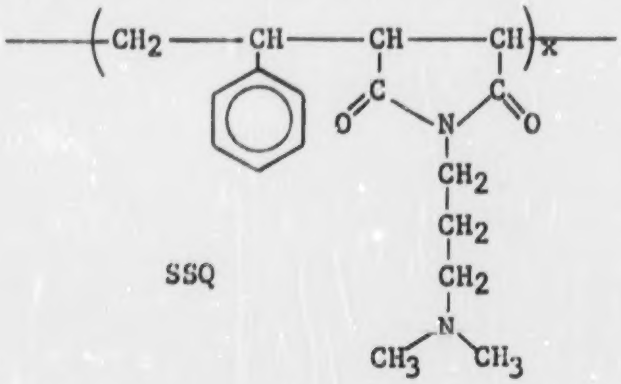
1.0 INTRODUCTION

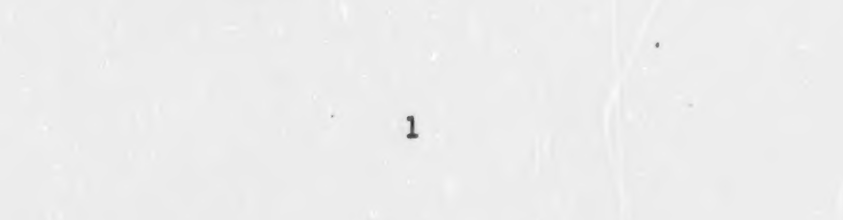
In a previous report[1] under the present contract the requirements for a satisfactory sorbent for removal of SO_2 from waste gases were established, and promising materials were selected for further study and for incorporation into fiber. A styrene-dimethylaminopropyl maleimide copolymer (SSQ) was selected as the most promising material for further work because of its high SO_2 capacity, regenerability, cospinnability with fiber-forming polyolefins and stability toward oxidation and other side reactions.



SSQ

The behavior of this material as a SO_2 sorbent was examined in detail. The SO_2 capacity as a function of temperature and SO_2 concentration in the gas phase was determined, and was found to follow the Langmuir adsorption isotherm. It was found that SO_2 could be essentially completely desorbed from the material by flushing with nitrogen at elevated temperature (95°C). The presence of water vapor in the gas stream appeared to increase the SO_2 capacity of the material, but no quantitative information on the relative amounts of water and SO_2 sorbed in the process was obtained in that phase of the work.

Another candidate sorbent, polyethylenimine (PEI), was also evaluated in some detail. This material was of interest because of its low equivalent weight which gives it a potential SO_2 capacity of about 1.47 g SO_2/g PEI assuming a 1:1 reaction of SO_2 with the basic nitrogen. Although high capacities were obtained experimentally, regenerability was very poor. We postulated that the poor regenerability was due to the large percentage of primary and secondary amino groups in the material which are much more susceptible to irreversible side reactions than tertiary amino groups. Further work with polyethylenimine derivatives, in which substantially all of the amino groups were to be converted to tertiary amino, was planned.



PEI

Polypropylene fibers containing SSQ and PEI were spun, chiefly to determine the feasibility of spinning such fibers. Fibers containing as high as 12% PEI and 10% SSQ were spun using conventional melt-spinning techniques, and indications were that considerably higher loadings could be achieved.

In the work described in the present report basic sorbents were evaluated with particular emphasis on (1) selectivity toward SO_2 in the presence of other flue gas constituents (2) stability in the operating environment (3) high temperature capacity and (4) reversibility.

Two waste gas compositions were specified for evaluation of sorbents and fibers:

Component	Volume Per Cent I	Volume Per Cent II
N_2	74.9	81.7
CO_2	14.7	-
H_2O	7.25	2.6
O_2	2.8	4.2
SO_2	0.3	11.5
NO_x	0.05	-
Fly Ash	0.2 (wt)	3.0 (wt)

Composition I approximates a coal-burning power plant flue gas and composition II approximates one type of smelter gas. All of the work in the present report was done with composition I for the following reasons:

1. The need for SO_2 removal methods for flue gases is more pressing.
2. SO_2 removal from composition I is the more difficult case, since the SO_2 concentration is lower, thus requiring a sorbent with greater affinity for SO_2.
3. Case I presents the greater number of possible complications due to side reactions with other reactive gases (NO_x, O_2, CO_2) which can lead to regenerability problems.

We felt that if gases of composition I could be successfully dealt with, this process could be readily adapted to gases of composition II.

Fly ash was left out of composition I because of experimental difficulties in bench-scale testing. Future work, on a larger scale, would include fly ash in its gas composition.

2.0 PHYSICAL PROPERTIES OF FIBERS

One of the chief objectives of the present program was to produce fibers containing as high a level of the active sorbent polymer as possible, while maintaining adequate fiber physical properties so that the fiber could be fabricated into a variety of final assemblies, such as belts made of woven or knitted material.

Although several parameters are recognized as being important in obtaining maximum SO_2 capacity and rate of sorption, high loading of the amine-containing polymer in the fiber was found to be the most important. Polypropylene fibers containing from 8.3% to 60.0% SSQ were spun and evaluated. Although the physical properties of the fibers (tenacity, ease of spinning etc.) diminished with increased SSQ loading, even at 60% SSQ the tensile strength of the fiber was well within the range of many commercial textile fibers and should enable processing into knits, felts, woven goods etc. on conventional textile machinery. In addition, there is no apparent reason why such fibers cannot be spun on large-scale commercial melt extruders.

2.1 Polypropylene Fibers

The range of SSQ content, denier, draw ratio and tenacity of a number of polypropylene fibers spun in this program are shown in Table I.

Table I

Physical Properties of Polypropylene-SSQ Fibers

Fiber Code	% SSQ	Denier per Filament Undrawn	 Drawn	Draw Ratio	Tenacity of Drawn Fiber (g/denier)
3C	8.33				
112C	14.25	78.2		7:1	5.69
119A	22.2	65.7	11.0	6:1	4.10
124A	33.3		9.1	5.5:1	
124B	42.2		11.0	5:1	3.0
129A	50.0		18.4	3.5:1	1.40
129B	50.0		17.5	3:1	1.39
129C	60.0		18.3	3:1	0.92
129D	60.0		18.4	3:1	1.40

2.1.1 Effect of Temperature on Physical Properties

In order to ensure that the fibers prepared in this program retained sufficient strength at temperatures in the range at which the process would be carried out, the tensile strength of selected fibers was tested at room temperature, 55°, 75°, and in one case 100°C.

Table II

Effect of Temperature on Strength Properties of Polypropylene-SSQ Fibers

Fiber	%	Tenacity (g/denier)							
Code	Sorbent	R.T.	55°C	75°C	100°C	% Elongation			
129A	50.0	1.40	1.46	1.23	1.02	22.4	30.2	51.8	69.8
129B	50.0	1.39	1.12	0.98		20.9	25.0	32.5	
129D	60.0	1.40	1.41	1.31		23.0	40.1	51.2	
112C	14.25	5.69	4.18	3.88		12.9	23.1	26.6	

The data in Table II shows that although fiber strength does decrease with increasing temperature as expected, there is no evidence of severe failure, and the strength is sufficient to allow the use of these fibers in practically any desired assembly. In addition, fiber assemblies could include reinforcement with a strong temperature-resistant fiber if necessary.

A more important potential problem is the fusion of the fibers at elevated temperatures. Although sorptions and regenerations carried out at 125°C have shown that fiber fusion does not occur at this temperature, we determined the maximum temperature attainable without occurrence of fiber fusion for several fibers.

A test was devised in which fiber samples were wound on a pyrex glass tube so that a multiple layer of fibers resulted, i.e., >4 layers. An apparatus was set up so that the fiber-wound glass tube could be inserted into a pyrex test tube, which in turn was immersed in a heated, stirred, oil bath. The "non-stick" temperatures were determined by heating the fiber samples at specific temperatures and periods of time, e.g., 164°C for 45 minutes, 144°C for 60 minutes, or 155°C for 60 minutes. At the end of the period of time at each temperature, the fiber-wound pyrex tube was removed from the test tube and allowed to cool. The appearance of the fiber was noted and its capability of being removed from the tube by unwinding was determined. The results of the tests are given in Table III.

Table III

Effect of Temperature on Physical Properties of Polypropylene-SSQ Fibers

Fiber Sample	Temp. (°C)	Time (min.)	Appearance and Effect
129D (60% SSQ, drawn 3:1)	164	45	All samples became yellow or brown with fusion
129D (60% SSQ, undrawn)	164	45	
124B (42% SSQ, drawn 5:1)	164	45	
124B (42% SSQ, undrawn)	144	60	No effect
112C (12.5% SSQ, drawn 7:1)	144	60	
112C (12.5% SSQ, undrawn)	144	60	
129D (60% SSQ, drawn 3:1)	144	60	
129D (60% SSQ, drawn 3:1)	151-155	60	
112C (12.5% SSQ, drawn 7:1)	151-155	60	
112C (12.5% SSQ, undrawn)	151-155	60	
124C (42% SSQ, drawn 4:1)	151-155	120	Some sticking evident
124C (42% SSQ, undrawn)	151-155	120	
129D (60% SSQ, drawn 3:1)	151-155	120	

The data above shows that a polypropylene fiber containing 60% SSQ can be exposed to a maximum temperature of 155°C in air for at least one hour without fusion or apparent deleterious effects.

Since the maximum temperature used in any part of the sorption-regeneration cycle would not exceed about 125°C, a margin of about 30°C is available to allow for temperature fluctuation without the danger of serious degradation of the fibrous assembly.

2.1.2 Effect of Sorption-Regeneration Cycling on Physical Properties of Polypropylene-SSQ Fibers

Samples of polypropylene-SSQ fibers were carried through several sorption-regeneration cycles with the SO_2-N_2 mixture and with simulated flue gas, and were then tested for tensile strength and elongation. The results (Table IV) show that there is only a small effect upon the fiber properties, and that degradation of the physical properties of the fibers during use probably will not be a major problem.

Table IV

Effect of Sorption-Regeneration Cycling upon Physical Properties of Polypropylene-SSQ Fiber

Pull No.	Breaking Force, #	% Elongation	Tenacity, g/denier
	(IB) 10 cycles simulated flue gas		a)
1	1.113	865.5	0.986
2	1.190	850.0	1.05
3	1.079	837.0	0.956
4	0.907	671.0	0.804
5	1.040	725.0	0.921
6	1.015	772.5	0.899
		786.8	0.937
	(IA) 14 cycles SO_2-N_2-H_2O		b)
1	0.81	635	0.718
2	0.86	614	0.762
3	0.78	741	0.691
4	1.06	752	0.939
5	0.79	710	0.700
		690	0.762
	Untreated fiber		b)
1	0.84	821	0.744
2	0.87	821	0.771
3	0.92	778	0.815
4	1.02	818	0.904
5	1.05	777	0.930
		803	0.833

Undrawn polypropylene fiber containing 8.3% SSQ

8 filament, 512 denier. Data obtained on Instron tester.

a) 2 in. sample, 2# pull, 10"/min. crosshead speed

b) 2 in. sample, 10# pull, 10"/min. crosshead speed

2.2 Nylon Fibers

To evaluate materials other than polyolefins as matrix polymers, three nylon-SSQ fibers were spun. The compositions, in per cent by weight, are given in the following table.

Table V

Nylon-SSQ Fibers

Fiber	% SSQ	% Nylon
113A	33.3	66.5 (Zytel 42)
113B	49.9	49.9 (Zytel 42)
113C	24.9	49.9 (Zytel 101)

The tensile strength of all three fibers was found to be very low - so low that spinning the fibers was difficult. Instron data (breaking force, % elongation and tenacity) were not taken because of the low tensile strengths. It was obvious that such fibers had **insufficient** strength to permit satisfactory fabrication into an assembly suitable for sorption of SO_2 from waste gases. In comparison, the mechanical properties of polypropylene-SSQ fibers were quite satisfactory. It is apparent that a polyolefin, such as polypropylene, is a more satisfactory polymer for the formation of SSQ-containing fibers having good mechanical properties, than is a polyamide such as nylon.

3.0 SO_2 CAPACITY OF FIBERS

The SO_2 capacities of selected polypropylene fibers containing various levels of SSQ were measured after 4 hours exposure to simulated flue gas. As shown in Table VI below, fiber containing 60% SSQ had a capacity of 3.4% at 4 hours with a flow rate of gas through the sample such that essentially all of the SO_2 was removed from the gas stream (cf. Fig. 1, Table VII). The estimated maximum SO_2 capacity that the fiber could have, with sufficient exposure time to the flue gas, is 11.5% (calculation based on its SSQ content). It is not expected, however, that the full capacity of this fiber could be utilized in a practical system, since the rate of sorption becomes slower with increasing degree of saturation.

Table VI

SO_2 Capacity of Polypropylene-SSQ Fibers

(53°C, Simulated Flue Gas, 4 Hour Exposure)

% SSQ	g SO_2 + H_2O/g fiber	g SO_2/g fiber	Average g SO_2/g fiber/hr	Estimated Saturation g SO_2/g fiber
8.13	0.0099	0.0079	0.0020	-
22.2	0.029	0.023	0.0058	0.042
42.2	0.038	0.030	0.0093	0.080
60.0	0.042	0.034	0.011	0.115

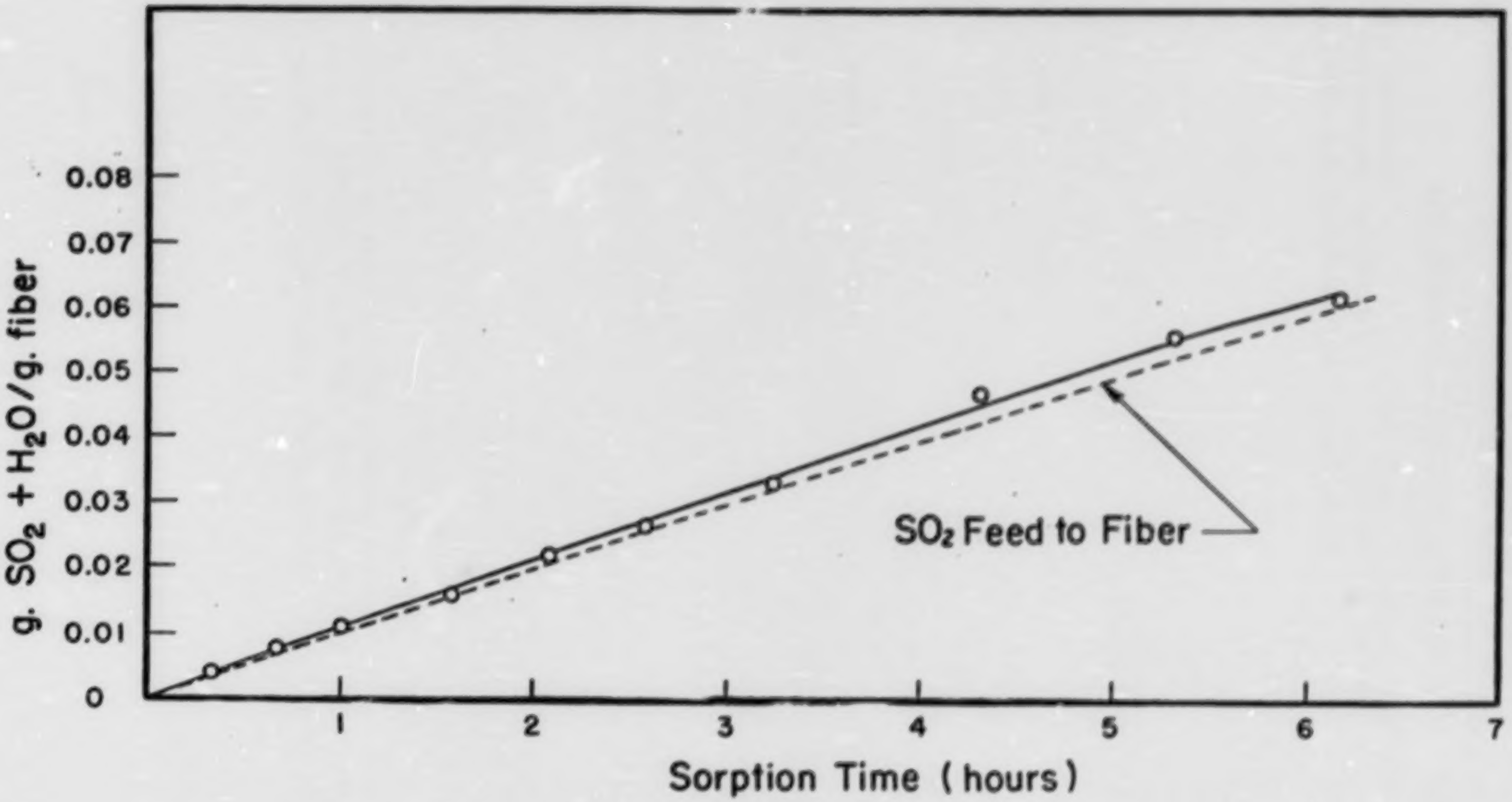


Fig. 1 Rate of sorption of SO$_2$ from simulated flue gas on 60% SSQ-polypropylene fiber at 55°C. Flow rate: 121 ml/min. Space velocity: 2056 hr.$^{-1}$

Table VII

Sorption-Regeneration of Wet, Simulated Flue Gas on SSQ-Polypropylene Fiber 129D (drawn 3:1) (60% SSQ)

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	PPM SO_2 in Effluent Gas During Sorption	Regeneration Time (hrs.)	Remaining after Regeneration (g/g fiber)
1	0.33	0.0043			
	0.66	0.0074			
	1.00	0.0110			
	1.58	0.0154			
	2.08	0.0214			
	2.58	0.0268			
	3.23	0.0333			
	4.30	0.0463			
	5.32	0.0551			
	6.17	0.0619			
				15.5**	0.0064
2	0.33	0.0039			
	0.66	0.0070			
	1.00	0.0095			
	1.50	0.0104			
	2.85	0.0086			
	2.85	0.0151***			
				3.23	-0.0003
3	0.33	0.0033			
	0.66	0.0060			
	1.00	0.0077			
	1.50	0.0085			
	2.88	0.0081			
	2.88	0.0143***			
				1.68	0.0000
4	3.13		100.0		
	3.22		180.0		
	4.00		450.0		
	4.17		580.0		
	4.93		1,190.0		
	5.95		1,580.0		
			4,910.0****		

* g SO_2 + H_2O/g fiber

** Flow rate 21.2 ml./min.; Temperature 80°C

*** Based on original starting weight. Other weights in cycles 2 & 3 are based on preceding cycle regeneration weight.

**** Feed gas according to chromatograph. Actual SO_2 conc. 3100 ppm.

Table VII (Con't.)

Conditions:

Sorbent: 6.4686 g, drawn (3:1), SSQ-Polypropylene Fiber 129D (60% SSQ)

Sorption:

Feed Gas: Simulated Flue Gas SO_2 0.31%; NO 0.041%; O_2 2.70%; CO_2 14.00%; H_2O 8.0%; N_2 75.0%

Flow Rate:	121 ml./min.
Temperature:	Cycles 1 & 4 55°C Cycles 2 & 3 95°C

Regeneration:

Feed Gas:	dry N_2
Flow Rate:	271 ml./min. (except in cycle 1. See **)
Temperature:	95°C (except in cycle 1. See **)

3.1 Effect of Increased SSQ Level upon SO_2 Capacity

A comparison of the sorption data, on both g SO_2/g SSQ and g SO_2/g fiber basis, of a fiber containing 14.25% SSQ and drawn 7:1 with an undrawn 8.33% SSQ fiber yields interesting information on the effects of SSQ level. Comparative data are given in Table VIII.

Table VIII

SO_2 Sorption of Polypropylene-SSQ Fibers (6 cycles)

Fiber	g SO_2 + H_2O/g fiber	g SO_2 + H_2O/g SSQ
112C (14.25% SSQ; drawn 7:1)	0.0335 (a)	0.2348 (c)
3C (8.33% SSQ; undrawn)	0.0111 (b)	0.1345 (d)

The ratio (a)/(b) is 3.029, and ratio (c)/(d) is 1.7455; but the ratio SSQ in 112C/SSQ is 3C is 1.710. The (a)/(b) ratio which represents the total effect of the two parameters (SSQ level and fiber drawing) actually is the product of the other two ratios: (c)/(d) representing the effect of fiber drawing or increased permeability, and the SSQ level ratio, 1.710. (1.7455 x 1.710 = 2.985).

From the comparison of fibers 112C and 3C one might attribute the significant increase in SO_2 capacity over what is expected from the increased SSQ level alone to the increased (2.64 fold) surface area of the drawn fiber. However, experiments on fibers containing polyethylene oxide (Section 3.3) indicate that drawing has only a small effect upon rate and capacity, and the chief effect in this fiber is probably permeability to SO_2 because of the increased SSQ level.

3.2 Effect of Temperature on Sorption Capacity

In a typical power plant, the flue gas is discharged at about 300°F (150°C). It is desirable to carry out the sorption process at temperatures close to this so that the need for cooling of the gas (with the attendant costs) is minimized. In order to establish the practical maximum temperature at which the sorption process could be carried out, the saturation SO_2 capacity of a polypropylene fiber containing 60% SSQ was determined at several temperatures with simulated flue gas. Data are shown in Table IX.

Table IX

Temperature Effect on Sorption Capacity of Polypropylene-60% SSQ Fiber

Sorption Temperature (°C)	Weight Sorbed (g SO_2 + H_2O/g Fiber)
65	0.039
75	0.022
85	0.014
95	0.0093
110	0.0025
125	0.0007

The SO_2 capacity decreases rapidly with increasing temperature. This is probably a result of two effects: first, the usual behavior of Langmuir-type sorptions is for the capacity of the sorbent to decrease with increasing temperature, and secondly, the amount of water sorbed along with the SO_2 at higher temperatures is much smaller than at lower temperatures (cf. Sec. 3.8). The sorptions at 95° and above are essentially "dry" sorptions, and it has been shown that the SO_2 capacity of SSQ under dry conditions is considerably less than in the presence of water vapor.

While the low capacity of the sorbent fiber at temperatures around 95°C and above in itself is a distinct disadvantage, this adverse effect is partially offset by the beneficial effect of such temperatures on the accumulation of nonthermally desorbable (NTD) material in the sorbent fiber. (The relationship of temperature and the accumulation of NTD material is discussed in Sec. 4.2.2.) Since relatively little NTD material is formed at temperatures above 95°C, the need for periodic chemical regeneration of the sorbent fiber to remove NTD material is greatly reduced, and the effective life of the sorbent is greatly prolonged. However, as mentioned earlier, there is some SO_3 normally present in flue gas which will lead to accumulation of sulfate (NTD) in the fiber, thereby partially offsetting the advantage of reduced

NTD formation in the sorbent at 95°C. A possible method of dealing with the SO_3 in the flue gas may be to either pre-treat the gas with a particulate sorbent such as limestone or other material which reacts much more readily with SO_3 than it does with SO_2, or to allow the sorbent fiber to remove the SO_3 as well as SO_2 and increase the chemical regeneration treatment to the required level.

3.3 Hydrophilicity of Sorbents

Since the presence of water vapor in SSQ and in SSQ-polypropylene fiber caused a significant increase in SO_2-sorption capacity(1) it seemed probable that the incorporation of a hydrophilic material in a polypropylene-SSQ fiber would effect a further increase in the SO_2 sorption capacity. Two such fibers were spun and evaluated.

Both of these fibers, 112A and 112B, contained polypropylene, 8.3% SSQ, stabilizers, and poly(ethylene oxide) (Polyox WSR 301). Fiber 112B also contained a proprietary spinning aid. The denier of fiber 112A was 439.2 (7 filament) and of fiber 112B, 702 (8 filament). Both fibers were quite satisfactory as to tensile, had high luster, and could be drawn readily.

A comparison of the SO_2 sorption data from the first four cycles of fiber 112A with the sorption data from cycles 3-6 inclusive of control fiber 3C is given in Table X.

Table X

Effect of Hydrophilic Additive on Sorption Capacity

Fiber	g SO_2 + H_2O/g fiber
112A (8.33% SSQ; 8.33% Polyox)	0.0209
3C (8.33% SSQ; no Polyox)	0.0128

Since all other parameters in the two sorption experiments were the same, the higher sorption by fiber 112A must be attributed to its Polyox content. This increase may be due to any one, or a combination, of the following possible causes: (1) the hydrophilicity of Polyox (2) SO_2 sorption by Polyox (3) improved SO_2 permeability of the fiber, imparted by its Polyox content.

In regard to possible cause (1), a comparison of the percentages of water desorbed from fibers 112A and 112C (see Section 3.8) indicates that the Polyox in fiber 112A effected an increase of 4% in water sorption. This effect may be due to the hydrophilicity of Polyox but is much smaller than expected. The H_2O-sorption capacity of Polyox alone (see following Section) was also found to be unexpectedly small. In view of these data there is considerable doubt that the hydrophilicity of Polyox, per se, has any significant effect upon the SO_2-sorption capacity of an SSQ fiber.

In order to determine the validity of possible cause (2), the sorption of SO_2 + H_2O vapor, and H_2O vapor alone, on Polyox WSR-301 was investigated. A mixture of Polyox and Chromosorb W, containing 16.6% of Polyox, was used as sorbent. In determining water sorption, the feed gas was nitrogen plus 8.0% water vapor; and for the determination of SO_2 + H_2O sorption, the feed gas was a mixture of 0.77% SO_2, 8.0% water vapor, and 91.23% N_2. Sorption temperature was 55°C, and regenerations were at 95°C. Dry nitrogen was the feed gas during regenerations. All weight changes in the sample during the 4 sorptions and 3 regenerations were quite samll - ranging from 0.00 to 4.9 milligrams. It is obvious from these data that the SO_2-sorption and H_2O-sorption capacities of poly(ethylene oxide) are both very low under these conditions. Therefore it may be concluded that neither of these sorptions caused the observed improvement in SO_2-sorption by SSQ fibers effected by the addition of poly(ethylene oxide). The improvement is probably due to increased permeability of the fiber to SO_2 (cause (3) above).

As supporting evidence for the validity of cause (3), Mr. Charles K. Neulander of General Electric Company in his presentation at the New Process Development Section Contractor's Meeting in Cincinnati, Ohio December 12-13, 1968 stated that of the liquid membranes tested for SO_2 permeability, poly(ethylene) glycol was the best. Since poly(ethylene glycol) in a liquid form is simply a lower molecular weight Polyox, it is quite reasonable to assume that the Polyox WSR-301 in fiber 112A is also readily permeated by SO_2 and imparts this property to the fiber. Although increased permeability of a fiber to SO_2 is a very desirable effect imparted by Polyox, the use of Polyox for this purpose is not advantageous, since high levels of SSQ also cause this effect. (See discussion of the relationship of SSQ levels to permeability of a fiber in Section 3.1). High levels of Polyox will increase the SO_2-sorption capacity of fibers because of improved permeability only, while high levels of SSQ in a fiber will improve its SO_2-sorption capacity in two ways; (1) by increasing permeability and (2) by increasing the weight ratio of SO_2-sorbent to host polymer.

3.4 Sorption Capacity of Polypropylene Fiber

Since polypropylene is the host polymer in which the sorbent is dispersed, a "blank" run to determine the SO_2 + H_2O capacity of polypropylene fiber without sorbent was carried out.

The capacity of a sample of an undrawn polypropylene fiber prepared by the same procedure as used for the sorbent-containing fibers was determined over 4 sorption-regeneration cycles with a gas mixture containing 7,700 ppm SO_2, 8% H_2O vapor, and nitrogen. Temperature during sorption and regeneration was 55°C and 95°C, respectively. The results are shown in Table XI:

Table XI

SO_2 and H_2O Capacity of Polypropylene Fiber without Sorbent

Cycle No.	$SO_2 + H_2O$ Capacity (g/g fiber)
1	0.0005
2	0.0005
3	0.0005
4	0.0006

Since the capacities of SSQ-containing fibers under the same conditions are much higher, e.g., a 14.3% SSQ fiber, drawn 7:1 has a capacity of 0.0280 g/g, the contribution of the polypropylene to the sorption capacity of the fiber is negligible.

3.5 Effect of Drawing

Comparative data on a fiber (22.2% SSQ, 22.2% Polyox WSR-301 and 55.6% polypropylene), both drawn and undrawn, showed that the drawing caused about a 10% increase in both the sorption rate and the final SO_2-capacity of the fiber. The capacities ($SO_2 + H_2O$) and sorption rates of the drawn and undrawn fiber were determined at 55°C. Data are given in Tables XII and XIII. Comparative data on fiber 119C, drawn and undrawn, are given in Table XIV.

Table XII

Sorption-Regeneration of SO_2-H_2O Vapor on

SSQ-Poly(ethylene oxide)-Polypropylene Fiber 119C (Drawn 5.5:1)

Cycle No.	Total Elapsed Sorption Time, Min.	Gain During Sorption, g/g		Remaining After Regeneration, g/g
1	174	0.2369*		0.0081
2	21	0.0868	**	
	41	0.1221		
	61	0.1430		
	91	0.1663		
	121	0.1914		
	151	0.1995		
	211	0.2141		
	250	0.2172		
	310	0.2432		
	341	0.2590		
	402	0.2530		
	462	0.2514		
	462	0.2595*		0.0908

*g $SO_2 + H_2O$/g SSQ, based on starting weight of sample

**g $SO_2 + H_2O$/g SSQ, based on weight of sample after first regeneration

Table XII (cont.)

Conditions:

Sorbent: 4.2950 g sample of drawn (5.5:1), SSQ-Polyox WSR 301 - Polypropylene Fiber (22.16% SSQ; 22.16% Polyox) 119C

Sorption:

Theoretical	0.2221 g SO_2/g SSQ
Feed Gas	SO_2 0.77%, H_2O 8.0%, N_2 balance
Flow Rate	271 ml./min.
Temperature	55°C

Regeneration:

Dry N_2; 271 ml./min.; 95°C

Table XIII

Sorption-Regeneration of SO_2-N_2-H_2O Vapor on SSQ-Poly(ethylene oxide) - Polypropylene Fiber 119C (Undrawn)

Cycle No.	Total Elapsed Sorption Time, Min.	Gain During Sorption, g/g	Remaining After Regeneration, g/g
1	183	0.1411*	0.0125
2	22	0.0784	
	42	0.1107	
	62	0.1249	
	93	0.1355	
	124	0.1503	
	155	0.1585	
	186	0.1645 **	
	217	0.1817	
	278	0.1992	
	338	0.2072	
	410	0.2270	
	470	0.2368	
	500	0.2292	
	530	0.2277	
	530	0.2400*	0.0511

*g SO_2 + H_2O/g SSQ, based on starting weight of sample

**g SO_2 + H_2O/g SSQ, based on starting weight of sample after first cycle

Conditions:

Sorbent: 4.6071 g sample of undrawn SSQ-Polyox WSR 301-Polypropylene Fiber 119C (22.16% SSQ; 22.16% Polyox)

Sorption:

Theoretical	0.2221 g SO_2/g SSQ
Feed Gas	SO_2 0.77%, H_2O 8.0%, N_2 balance
Flow Rate	271 ml./min.
Temperature	55°C

Regeneration: Dry N_2; 271 ml./min.; 95°C

Table XIV

Effect of Drawing on SO_2 Sorption

Sorption Time (Hours)	Percent of Final Capacity Fiber 119C, Undrawn	 Fiber 119C, Drawn 5.5:1
1.0	52.73	55.21
2.0	63.48	73.91
2.5	66.91	77.04
3.5	76.72	82.60
4.66	84.12	88.88
5.66	87.51	100.0
7.8	100.00	
Final Capacity		
g SO_2 + H_2O/g fiber	0.0525	0.0574
g SO_2 + H_2O/g SSQ	0.2368	0.2589

The data given in Table XIV indicates that an increased rate of sorption was effected by drawing the fiber. The rate of SO_2 sorption by the drawn fiber was in the range of 5-16% faster than that of the undrawn fiber. A graphic comparison of the two rates is shown in Figure 2. The undrawn fiber required 2.2 hours longer to reach its maximum capacity than the drawn fiber. The faster sorption rate of the drawn fiber may be attributed to its greater (2.33-fold) surface area.

It is apparent from the data in the above table that a slight increase (9.3%) in the maximum SO_2 sorption capacity of the fiber resulted from drawing it. This increase in capacity is comparable in magnitude to the 5-16% increase in rate of sorption previously discussed. As in the case of the sorption rate, the increased SO_2 sorption capacity of the drawn fiber may be attributed to its greater (2.33 fold) surface area, and this effect more than counteracts any opposite effect due to an increase in orientation of the fiber. The increase in capacity and rate due to drawing is relatively small in comparison to the increased surface area of the drawn fiber, however.

3.6 Effect of Water Vapor on Sorption Capacity

In earlier work[1], the pronounced beneficial effect of moisture upon the SO_2 sorption capacity of amine sorbents, such as SSQ and poly(ethylenimine), was repeatedly observed. The importance of this effect merited detailed study. Relevant aspects which would contribute toward a complete understanding of the effect were therefore investigated. These studies included the gathering of quantitative data on the improvement in SO_2 sorption capacity in the presence of moisture, the relationship of fiber composition to this effect, the mechanism of sorption involved and the effect of moisture thereon, the relative amounts of SO_2 and H_2O sorbed, and the relationship of temperature, moisture, and type of sorption. The results

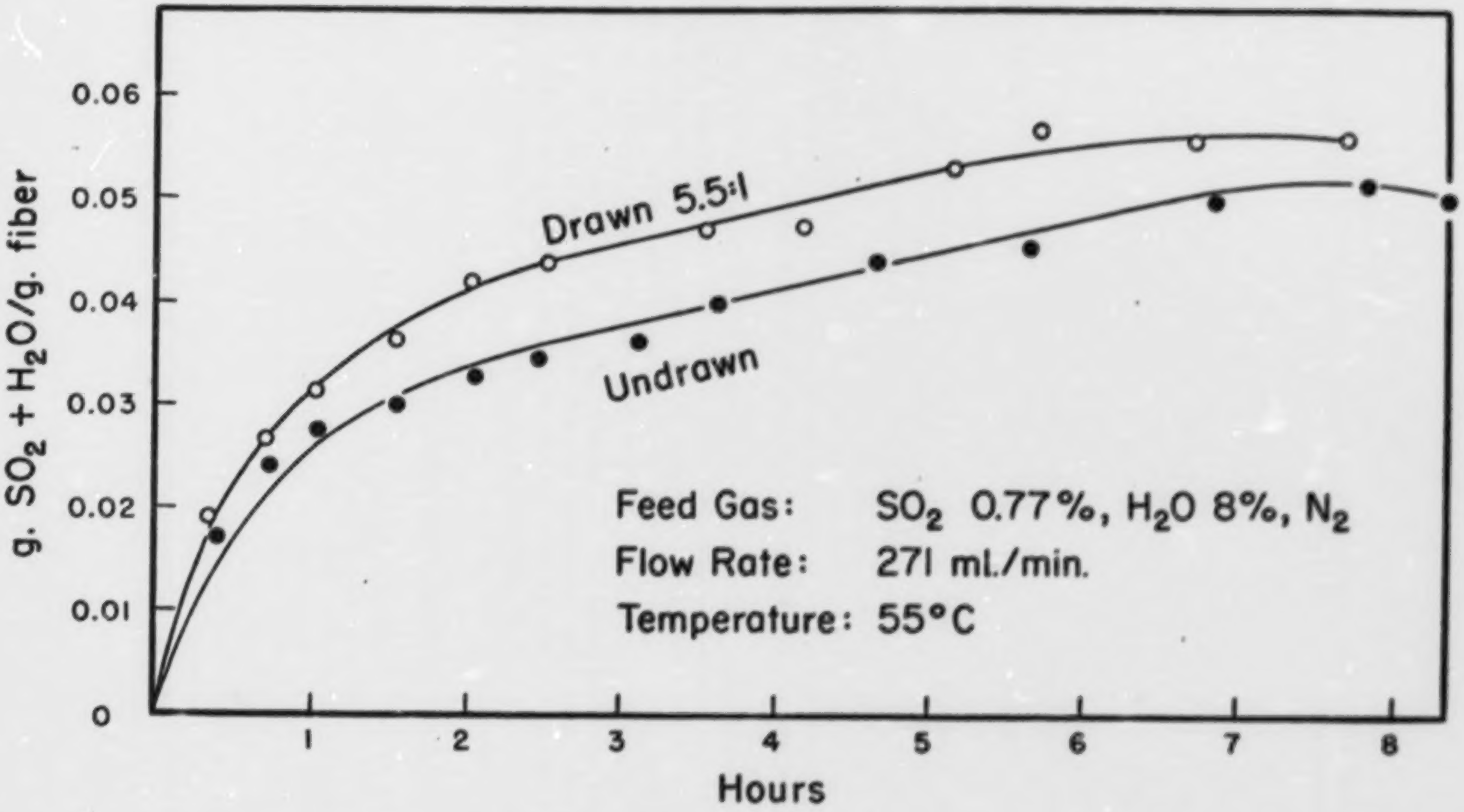


Fig. 2 - Ra[illegible] f sorption of SO_2-N_2-H_2O vapor by SSQ-Polyox-polypropylene fiber 119C (22.16% SSQ; 22.16% Polyox WSR-301)

of studies in these areas are discussed in the following sections. The data obtained are of considerable value in determing the optimum conditions for achieving the maximum SO_2 capacity of amine-containing fibers.

3.6.1 Details

A sample of SSQ was carried through 8 cycles of sorption-regeneration. Sorptions were at 55°C in a gas stream containing 7,700 ppm SO_2, 80,000 ppm H_2O, balance N_2. Regenerations were in dry N_2 at 95°C. Data are given in Table XV. The average sorption capacity of the sorbent during the 8 sorptions was 0.2048 g SO_2 + H_2O/g SSQ. In the absence of moisture, however, the SO_2-sorption capacity of SSQ is only 0.140 g SO_2/g SSQ, as calculated from the Langmuir isotherm[1]. The relative amounts of SO_2 and H_2O comprising the 0.2048 g were not determined.

Table XV

Sorption-Regeneration of SO_2-N_2-Water Vapor on SSQ

Cycle No.	Gain g/g	Remaining after Regeneration, g/g
1	0.2277	0.0092
2	0.2416	0.0128
3	0.2213	0.0167
4	0.2338	0.0192
5	0.2401*	0.0472
6	0.2352	0.0495
7	0.2212	(0.0491 @ 95°C) (0.0480 @ 115°C)
8	0.2200	0.0500

Conditions:

Sorption: 7,700 ppm SO_2, 80,000 ppm H_2O, N_2, 55°C, 271 ml./min.

Regeneration: Dry N_2, 271 ml./min., 95°C

*Sample allowed to stand at room temperature 18 hours before regeneration.

A chopped sample of an undrawn, polypropylene fiber containing 8.3% SSQ was carried through 14 cycles of sorption-regeneration. The first 12 sorptions were at 55°C in a gas stream containing 7,700 ppm SO_2, 80,000 ppm H_2O, balance N_2; and the last 2 sorptions were at 55°C in a gas stream containing no water (7,700 ppm SO_2, balance N_2). All regenerations were in dry N_2 at 95°C. Data are given in Table XVI. The average sorption capacity of the SSQ-containing fiber during the first 12 sorptions was 0.1058 g SO_2 + H_2O/g SSQ and 0.0088 g SO_2 + H_2)/g fiber. During the last 2 sorptions, in the absence of moisture, the average SO_2-sorption capacity of the fiber was 0.0373 g SO_2/g SSQ and 0.0031 g SO_2/g fiber.

Table XVI

Sorption-Regeneration of SO_2-N_2-H_2O Vapor on SSQ-Polypropylene Fiber

Cycle No.	Gain g/g	Remaining After Regeneration, g/g
1	0.0099	0.0006
2	0.0083	0.0016
3	0.0118	0.0031
4	0.0115	0.0036
5	0.0131	0.0041
6	0.0117	0.0041
7	0.0108	0.0038
8	0.0126	0.0040
9	0.0141	0.0052
10	0.0148	0.0053
11	0.0130	0.0055
12	0.0150	0.0053
13	0.0083) No H_2O vapor	0.0053
14	0.0085)	0.0053

Conditions: 4.3012 g undrawn 8.3% SSQ-polypropylene fiber

Sorption: SO_2 0.77%
H_2O 8.0 %
N_2 balance

Flow rate 271 ml./min., 55°C

Regeneration: Dry N_2, 271 ml./min., 95°C

In order to obtain some information on the relative amounts of SO_2 and water sorbed by the polypropylene-SSQ fiber (8.3% SSQ), an experiment was performed in which the first sorption was carried out in an SO_2-H_2O-N_2 gas mixture (10,000-121,700-868,300 ppm respectively), and three additional sorptions in an H_2O-N_2 mixture (121,700 and 878,300 ppm respectively). All regenerations were in dry N_2 at 95°C. Data are given in Table XVII. In the first cycle, a capacity of 0.1708 g

$SO_2 + H_2O$/g SSQ and 0.0142 g $SO_2 + H_2O$/g fiber was found, while in the absence of SO_2 in the last three cycles, the average capacity was 0.0105 g H_2O/g SSQ and 0.0009 g H_2O/g fiber.

Table XVII

Sorption-Regeneration of H_2O Vapor on SSQ-Polypropylene Fiber

Cycle No.	Gain, g/g	Remaining after Regeneration, g/g
1	0.0142	0.0019
2	0.0032	0.0021
3	0.0025	0.0016
4	0.0025	0.0014

Conditions: 4.0846 g 8.3% SSQ-polypropylene fiber

Sorption: Cycle 1 1.0% SO_2, 12.2% H_2O, balance N_2

Cycles 2-4 12.2% H_2O, balance N_2

271 ml./min., 55°C

Regeneration: dry N_2, 271 ml./min., 95°C

A chopped sample of an undrawn polypropylene fiber containing 8.3% SSQ and 8.3% poly(ethylene oxide) was carried through 7 sorptions and 6 regenerations. The first 5 sorptions were in an SO_2-H_2O-N_2 gas mixture (7,700-80,000-912,300 ppm respectively). Water vapor was excluded during the sixth sorption; and SO_2 was excluded during the seventh sorption. So, in the latter two sorptions, the feed gases were $SO_2 + N_2$ and $H_2O + N_2$, respectively. All regenerations were in dry N_2 at 95°C, and all sorptions were at 55°C except the fifth, which was at 95°C. Data are given in Table XVIII. In the presence of 8% water vapor in the first four sorptions, the average capacity was 0.2154 g $SO_2 + H_2O$/g SSQ and 0.0179 g $SO_2 + H_2O$/g fiber. In the absence of water vapor, in the sixth sorption, the capacity was only 0.0625 g SO_2/g SSQ and 0.0052 g SO_2/g fiber.

Table XVIII

Sorption-Regeneration of SO_2-N_2-H_2O Vapor on SSQ-Polyox (WSR-301) - Polypropylene Fiber

Cycle No.	Total Elapsed Sorption Time, min.	Gain During Sorption, g/g†	Remaining After Regeneration, g/g†
1		0.2269	0.0047
2		0.2526	0.0613
3		0.2993	0.0745
4	30	0.1668	-
4	37	0.2260	-
4	70	0.2249	-
4	103	0.2322	-
4	162	0.2541	-
4	357	0.2552	-
4	424	0.2570	-
4	483	0.2631	0.1215
5*		0.1592	0.1139
6**		0.1764	0.1154
7***		0.1738	-

Conditions:

Sorbent: 4.1210 g undrawn SSQ-Polyox WSR 301-polypropylene fiber (8.33% SSQ, 8.33% Polyox)

Sorption:

Theoretical 0.2221 g SO_2/g SSQ

Feed gas SO_2 0.77%
H_2O 8.0%
N_2 balance

Temperature 55°C
*95°C
**Dry (No H_2O vapor in feed gas)
***N_2-H_2O (No SO_2 in feed gas)

Flow rate: 271 ml./min.

Regeneration: Dry N_2, 271 ml./min., 95°C

†g/g represents g SO_2 + H_2O/g SSQ

3.6.2 Discussion

Pertinent data for comparison of SO_2-sorption capacities of SSQ in dry sorptions and in sorptions in the presence of water vapor are summarized in Table XIX. All sorptions were at 55°C. Capacities are given in g $SO_2 + H_2O$/g SSQ (or fiber), except as noted.

Table XIX

Comparison of "Dry" versus "Wet" Sorptions

Sample	% SSQ	% Polyox	Cycle No.	Feed Gas	% SO_2 in Feed Gas	% H_2O in Feed Gas	Capacity	
							g/g SSQ	g/g fiber
SSQ	100	0.0		1	0.77	8.0	(a) 0.2048	
Fiber 3C	8.3	0.0	1-12	1	0.77	8.0	(b) 0.1058	0.0088
Fiber 3C	8.3	0.0	13-14	2	0.77	-	(c) 0.0373*	0.0031*
Fiber 3C	8.3	0.0	1	3	1.00	12.2	(d) 0.1708	0.0153
Fiber 3C	8.3	0.0	3- 5	4	-	12.2	(e) 0.0105**	0.0009**
Fiber 112A	8.3	8.3	1- 4	1	0.77	8.0	(f) 0.2154	0.0179
Fiber 112A	8.3	8.3	6	2	0.77	-	(g) 0.0625*	0.0052*

* g SO_2

** g H_2O

Composition of Feed Gases:

1 SO_2 0.77%, H_2O 8.0%, N_2 91.23%

2 SO_2 0.77%, - N_2 99.23%

3 SO_2 1.0%, H_2O 12.2%, N_2 86.8%

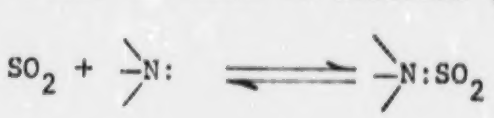
4 - H_2O 12.2%, N_2 87.8%

The beneficial effect of **moisture** upon the SO_2-sorption capacity of amine sorbents, which was repeatedly observed in earlier work, is again apparent in data given in this table. The "dry" capacity (c) of Fiber 3C was only 0.0373 g SO_2/g SSQ while the "wet" capacity was 2.84 times that amount, that is, 0.1058 g $SO_2 + H_2O$/g SSQ. Likewise, the dry capacity (g) of Fiber 112A was 0.0625 g SO_2/g SSQ, while the wet capacity (f) was 3.45 times that amount. Assuming that the bulk of the increase in weight sorbed by the wet gases in comparison to the dry sorptions was due to SO_2, (see Section 3.8 for a discussion of relative amounts of SO_2 and H_2O sorbed) it is evident that a strong synergistic effect is exerted by water vapor upon the sorption of SO_2. The somewhat better sorption capacities, both wet and dry, of Fiber 112A in comparison to Fiber 3C is probably due to the Polyox content of the former, since all other experimental conditions were alike for the two fibers. This seems to indicate a beneficial effect of a hydrophilic material such as Polyox upon the SO_2 capacity of an SSQ fiber. (See Section 3.3 for a discussion of this effect).

An increase in the concentration of SO_2 and H_2O in the feed gas (cf. capacities d and b for Fiber 3C) also caused a significant increase in the SO_2 capacity of the fiber. This was not an unexpected result since it had been observed in earlier work.

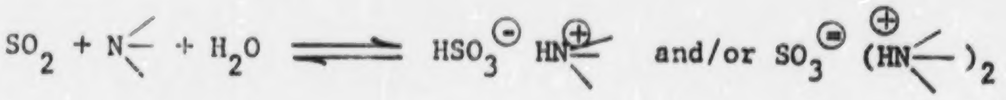
3.7 Mechanism of Sorption

The presence or absence of moisture in any SO_2-containing waste gas will determine the nature of the sorption which occurs (the effect of temperature is discussed in a later section). One sorption process which may occur between SO_2 and a tertiary amine such as SSQ can be called a "dry" sorption. It will occur in the absence of any appreciable amount of sorbed H_2O, and involves the formation of an anhydrous Lewis acid-base complex of SO_2 and amine, as shown in Reaction (A).



$$SO_2 + {>}N: \rightleftharpoons {>}N{:}SO_2 \qquad (A)$$

A second sorption process between SO_2 and a tertiary amine can occur only in the presence of sorbed H_2O, and may be called a "wet" sorption. This involves the formation of the sulfite and/or bisulfite salt of the amine, as shown in Reaction (B).



$$SO_2 + N{<} + H_2O \rightleftharpoons HSO_3^{\ominus}\ HN^{\oplus}{<} \text{ and/or } SO_3^{\ominus}\ (HN^{\oplus}{<})_2 \qquad (B)$$

Data which prove the occurrence of sorption by this mechanism are discussed in Section 3.8. In any given sorption of SO_2 from a waste gas by a tertiary amine sorbent, the amount of moisture present and sorbed will determine whether the sorption process will be of the "dry" or "wet" type, or a mixture of both types. The experimental data show greatly increased SO_2-sorption capacity of tertiary amines in the presence of water, indicating that SO_2 is sorbed as the bisulfite and/or sulfite salt ("wet" sorption) to a much greater extent that it is as the amine-SO_2 complex ("dry" sorption).

The type of sorption is controlled not only by the amount of moisture present and sorbed, but also by the temperature at which sorption occurs. This dependence on temperature will be discussed in a following section.

The type of sorption which occurs during any given SO_2 sorption has a very definite effect upon the ease and extent of regenerability of the sorbent. This effect is also discussed in a later section.

3.8 Relative Amounts of SO_2 and H_2O Sorbed

A determination of the relative amounts of SO_2 and H_2O sorbed by various fibers from an SO_2-H_2O-N_2 mixture, and from a simulated flue gas, was undertaken in order to obtain (1) the relative amount of water vapor required to effect the maximum SO_2 sorption capacity of the sorbent, (2) the sorbed SO_2:H_2O ratio under various conditions and (3) a clearer understanding of the mechanism of SO_2 sorption.

The relative amounts of SO_2 and H_2O sorbed at 55°C from an SO_2-H_2O-N_2 mixture, and at 95°C from a simulated flue gas, were determined by passing the effluent gas from each regeneration into a standardized iodine solution, and then titrating the unreacted iodine with standard thiosulfate solution. From the titration data, the amount of effluent (desorbed) SO_2 was calculated. The difference between the total weight desorbed and the weight of desorbed SO_2 was the weight of H_2O desorbed. Data on several desorptions, and the relative amounts of desorbed SO_2 and H_2O in each, are given in Table XX.

Table XX

Relative Amounts of SO_2 and H_2O Desorbed from Fibers

Fiber No.	% SSQ	% Polyox WSR-301	Feed Gas	Sorption Temp. °C	% H_2O in Feed Gas	Total Weight Desorbed	% of the Total Weight Desorbed	
							SO_2	H_2O
112A	8.3	8.3	1	55	8	0.0655	74.3	25.7
112C	14.3	0.0	1	55	8	0.0908	78.4	21.6
119C	22.2	22.2	1	55	8	0.1606	74.3	25.7
129D	60.0	0.0	2	95	8	0.0399	97.6	2.4
129D	60.0	0.0	3	95	16	0.0419	94.4	5.6
	1:1 SO_2 to H_2O molar ratio						78.05	21.95

Composition of feed gases:

1 SO_2 0.77%; H_2O 8.00%; N_2 91.23%

2 SO_2 0.31%; H_2O 8.00%; N_2 75.0%; O_2 2.70%; CO_2 14.00%; NO 0.041%

3 SO_2 0.28%; H_2O 16.00%; N_2 69.00%; O_2 2.48%; CO_2 12.88%; NO 0.038%

It is assumed that the quantities of SO_2 and H_2O desorbed on regeneration are the same as that sorbed during the sorption phase of the cycle. The only difference that could exist between the two quantities would be a result of irreversible sulfate (NTD) formation (cf. Sec. 4.2). This, however, would not affect the results significantly.

The data in Table XX indicate that the composition of the fiber had relatively little effect upon the ratio of SO_2 and H_2O desorbed. The difference in SSQ and Polyox levels in fibers 112A and 119C apparently had no effect whatever upon the SO_2:H_2O ratio but a comparison of the data on these two fibers with that of fiber 112C indicates that the presence of Polyox may have caused a 20% increase in the relative amount of H_2O desorbed. This effect was probably caused by the hydrophilic nature of Polyox. A discussion of hydrophilicity effects appears in Section 3.3. The change in the SO_2:H_2O ratio effected by the Polyox was not accompanied by any significant change in the SO_2-sorption capacity of the sorbent.

The temperature during the sorption exerted a much greater effect on the desorbed SO_2:H_2O ratio than the composition of the fibers. The temperature effect upon both the SO_2:H_2O ratio, and the type of sorption which occurs, is discussed in the following section.

A comparison of the ratios of SO_2:H_2O desorbed from fibers 112A, 112C and 119C after sorptions at 55°C, with the ratio of SO_2 and H_2O in a 1:1 molar adduct, shows that they are essentially the same. This experimental data substantiates the mechanism of "wet" sorption discussed in section 3.7. It is apparent then, that in SO_2 sorptions at 55°C from feed gases with a water content in the range found in flue gas, the SO_2 sorption will be chiefly, if not entirely, of the "wet" type, i.e., it will be sorbed as the bisulfite and/or sulfite salt of the tertiary amine sorbent. This sorption behavior will also be independent of the level of sorbent in the fiber.

The lower SO_2-sorption capacity of SSQ and SSQ fibers at temperatures of 95°C and higher has been observed repeatedly. It was thought probable that this effect was due, at least in part, to these sorptions being essentially "dry", that is, in the absence of an appreciable amount of sorbed H_2O. Two possible methods of avoiding this "dry" sorption might be (1) introducing more water in the gas stream and (2) using a more hydrophilic fiber as sorbent. The latter of these two methods is discussed in a following section. Data on a trial of the first method is shown in Table XX. A 100% increase in the percent of H_2O in the feed gas on fiber 129D caused a 100% increase in the amount of water desorbed, but the $SO_2 + H_2O$ sorption, i.e., the capacity of the fiber, was increased by only 5%. This result indicates that the introduction of larger amounts of H_2O in the feed gas, beyond the amount normally present in flue gases, is not effective in improving the SO_2 capacity of an SSQ fiber.

3.9 Relationship of Temperature, Moisture and Type of Sorption

The data tabulated in the preceding section show that in the sorptions at 55°C, both the SO_2 capacities of the fibers and the desorbed H_2O:SO_2 ratios were higher than in the sorptions at 95°C. These differences are attributed to a pronounced decrease in the amount of H_2O sorbed at the higher temperature. This lowered sorption of H_2O is a logical result of increasing the temperature almost to the boiling point of water. The change in the amount of H_2O sorbed, in turn, caused a change in the type of SO_2 sorption - from "wet" to "dry". And, as pointed out previously, SO_2 is sorbed as the amine-SO_2 complex ("dry" sorption) to a considerably less extent that it is as the bisulfite and/or sulfite salt of the amine sorbent ("wet" sorption). So, the final result of increasing the temperature to 95°C (or higher) is a considerable lowering of the SO_2-sorption capacity of SSQ-containing fibers.

3.10 Sorption Rates

A high rate of sorption is desirable for minimizing the amount of sorbent fiber required in the process. Factors which might be expected to affect sorption rate are: loading of sorbent polymer in the fiber, denier (thickness) of the fiber, water content of the fiber, and permeability of the fiber to SO_2.

The effect of an additive which probably functions through increasing the permeability is discussed in section 3.3. In addition, the effect of drawing the fiber is also discussed in section 3.5.

The rate of saturation of a fiber (124B) containing 42.2% SSQ, drawn 5:1 was tested in simulated flue gas at 55°C at flow rates of 21.2 and 275 ml. gas/min. These flow rates correspond to space velocities of 275 hr^{-1} and 3520 hr^{-1} respectively, based upon void fraction in the fiber bed (0.462). Data are shown in Table XXI. Figures 3 and 4 are plots of weight gain vs. time. Also shown on the graphs are plots of g SO_2/g fiber, fed to the fiber. The divergence from this line represents the SO_2 "leakage" through the bed. At a space velocity of 275 hr^{-1}, SO_2 removal is virtually complete, but at 3520 hr^{-1}, a large amount of leakage occurs.

Table XXI

Sorption-Regeneration of Wet, Simulated Flue Gas on Polypropylene-SSQ Fiber 124B (drawn 5:1) (42.2% SSQ)

Cycle No.	Total Sorption Time, hrs.	Gain During Sorption g/g Fiber	Remaining after Regeneration g/g Fiber
1	0.38	.0069	
	0.66	.0096	
	1.83	.0205	
	3.00	.0303	
	4.00	.0377	
	5.17	.0444	.0112
2	1.17	.0170	
	1.83	.0207	
	3.00	.0278	
	4.00	.0306	
	4.75	.0348	.0150
3	4.72	.0135	
	12.60	.0292	
	20.28	.0387	.0216

Conditions:

Sorbent: 5.3783 g drawn(5:1) Polypropylene-SSQ Fiber 124B (42.2% SSQ)

Sorption: Feed gas: Simulated Flue Gas

Flow rate: Cycles 1, 2, 271 ml./min. (space velocity 3518 hr^{-1})
Cycle 3, 21.2 ml./min. (space velocity 275 hr^{-1})

Temperature: 55°C

Regeneration:

Feed gas: dry N$_2$
Flow rate: 271 ml./min.
Temperature: 95°
Regeneration time: 3 hrs.

Fiber 129D (60% SSQ, drawn 3:1) was tested for capacity in simulated flue gas at 55° and 95°C with a flow rate of 121 ml./min. This flow rate corresponds to a space velocity of 2056 hr^{-1}, based upon void fraction in the fiber bed (0.353). Data are shown in Table XXII.

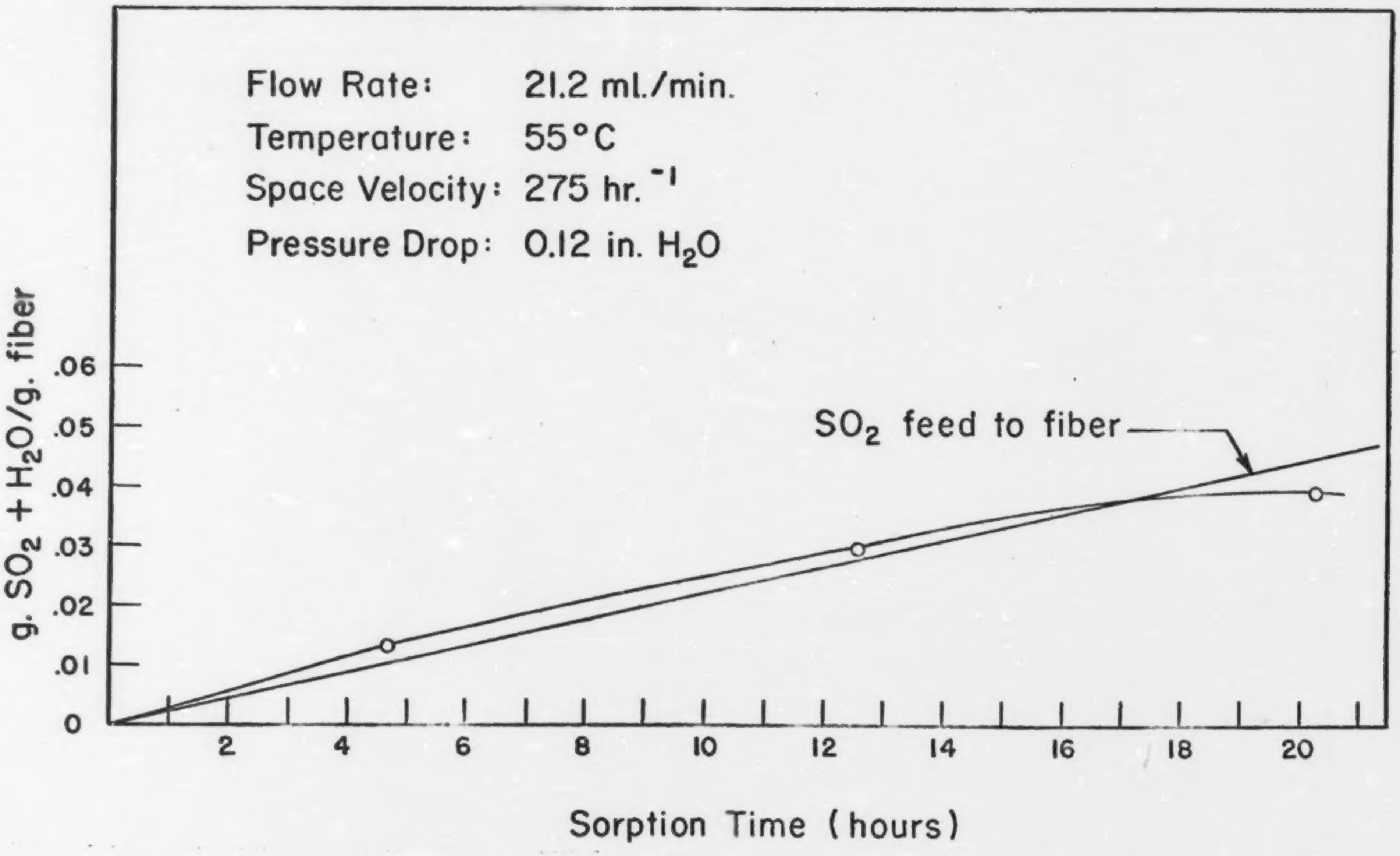


Fig. 3 - Sorption of wet simulated flue gas on SSQ-polypropylene fiber 124B (42.2% SSQ) Drawn 5:1 (Cycle No. 3)

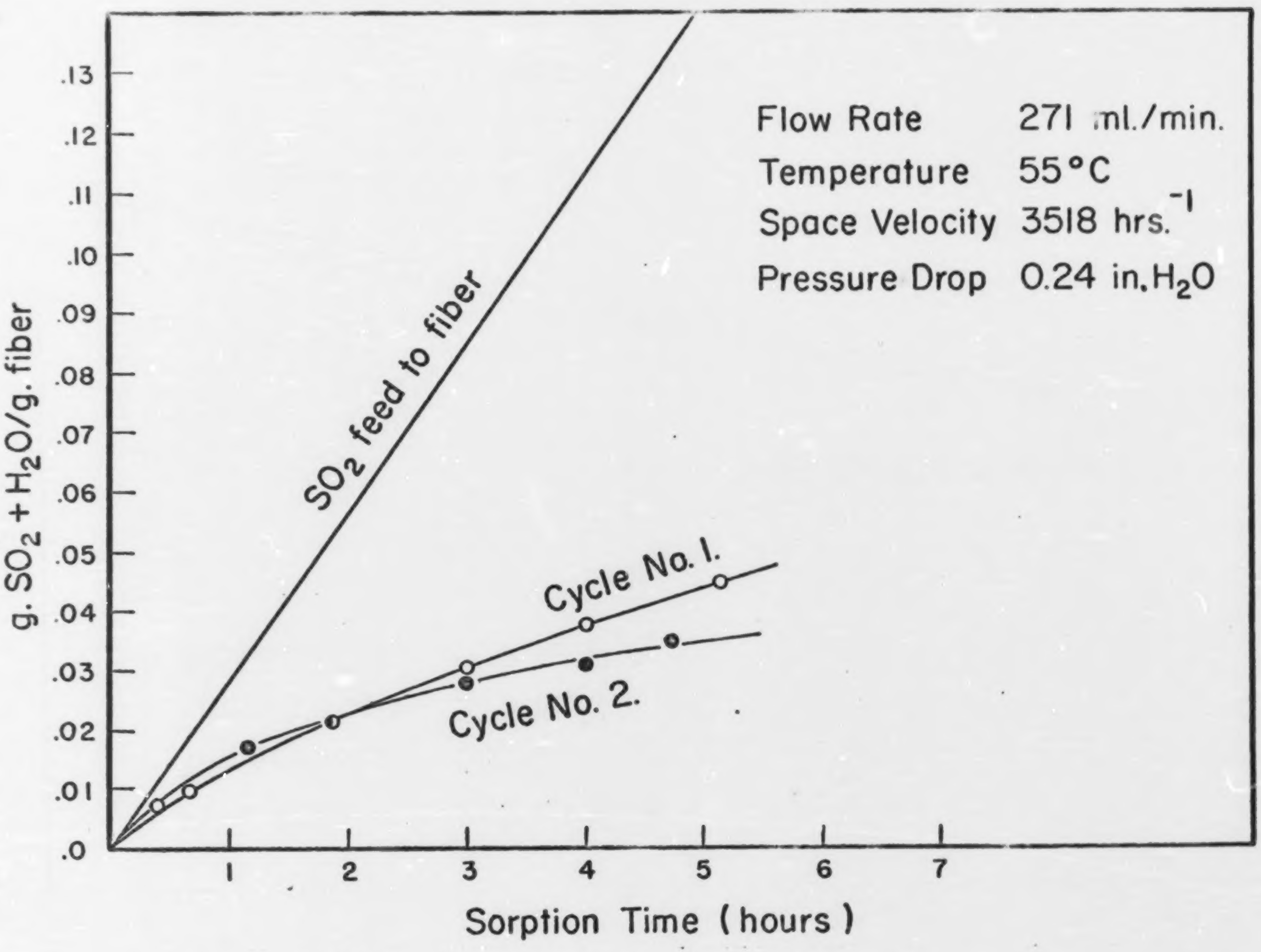


Fig. 4 - Sorption of wet simulated flue gas on SSQ-polypropylene fiber 124B (42.2% SSQ) (Drawn 5:1) Cycles No. 1, 2. ●

Table XXII

Sorption-Regeneration of Wet, Simulated Flue Gas on Polypropylene-SSQ Fiber 129D

(drawn 3:1)(60% SSQ)@ 55° and 95°C

Cycle No.	Sorption Time (hrs.)	Gain During Sorption(g/g)*	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
1	0.33	0.0043		
	0.66	0.0074		
	1.00	0.0110		
	1.58	0.0154		
	2.08	0.0214		
	2.58	0.0268		
	3.23	0.0333		
	4.30	0.0463		
	5.32	0.0551		
	6.17	0.0619		
			15.5**	0.0064
2	0.33	0.0039		
	0.66	0.0070		
	1.00	0.0095		
	1.50	0.0104		
	2.85	0.0086		
	2.85	0.0151***		
			3.23	-0.0003
3	0.33	0.0033		
	0.66	0.0060		
	1.00	0.0077		
	1.50	0.0085		
	2.88	0.0081		
	2.88	0.0143***		
			1.68	0.0000

* g $SO_2 + H_2O$/g fiber

** Flow rate 21.2 ml./min.; Temperature 80°C

*** Based on original starting weight. Other weights in cycles 2 and 3 are based on preceding cycle regeneration weight.

Figure 5 is a plot of weight gain vs. time. Also shown on the graph is a plot of the g SO_2/g fiber, fed to the sample. The divergence from this line represents the SO_2 "leakage" through the fiber bed. At 55°C (cycle 1), SO_2 removal from the feed gas was complete throughout a period of 6 hours. At 95°C (cycles 2 and 3), however, SO_2 leakage began after about 40 minutes and the SO_2 capacity of the fiber leveled off at its saturation capacity under these conditions of SO_2 concentration and temperature. The space velocity may be calculated by use

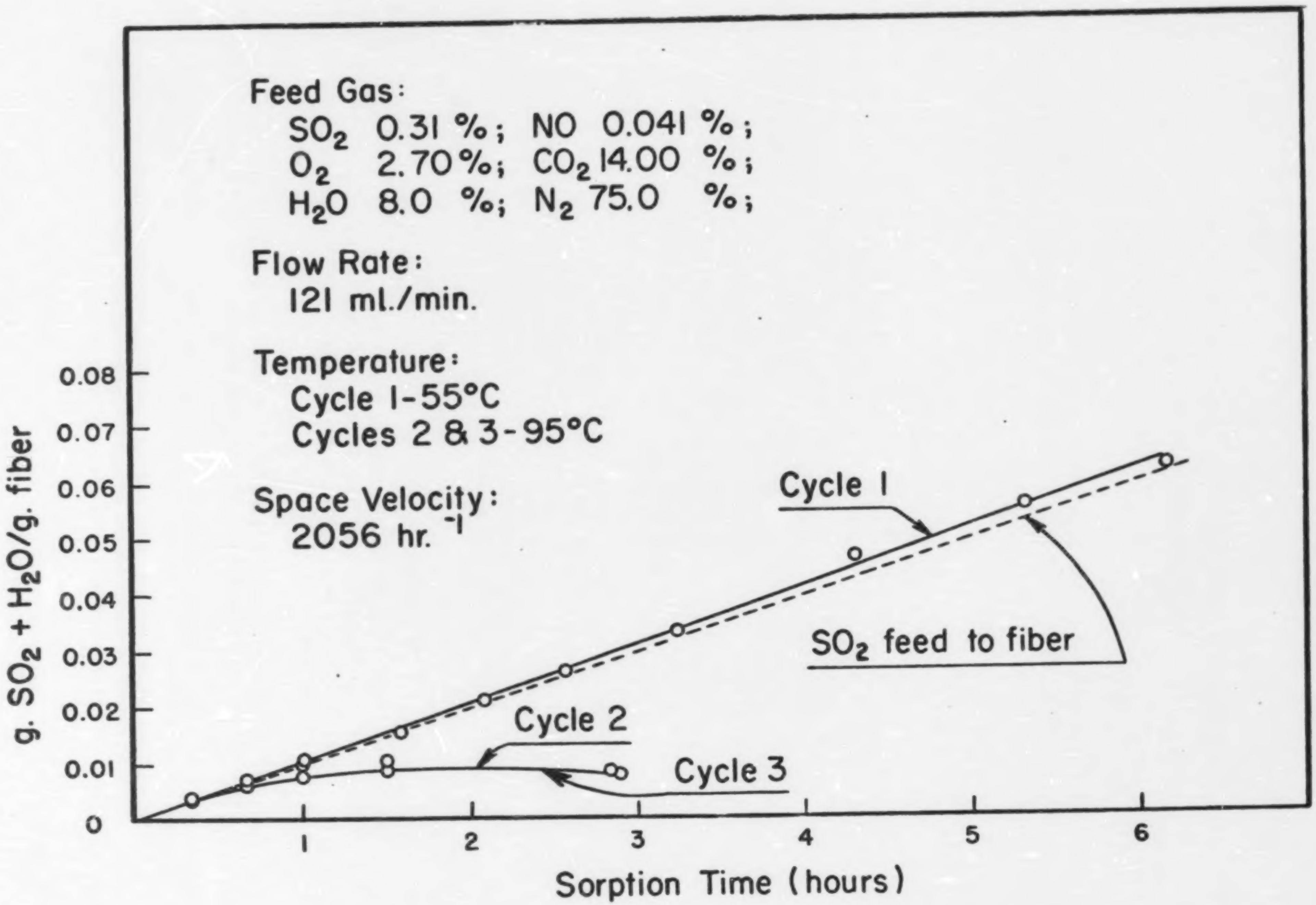


Fig. 5 - Rate of sorption of simulated flue gas on SSQ-polypropylene fiber 129D at 55° and 95°C (drawn 3:1; 60% SSQ).

of the following formula:

$$\text{space velocity} = \frac{\text{flow rate (ml./min.)}}{\text{total volume of sample holder (10 ml.)} - \text{weight of sample in gms. (assumed density = 1)}} \times 60 = \text{S.V.}(\text{hr}^{-1})$$

Since no change was made in the flow rate during the series of sorption-regeneration cycles, the space velocity remained constant throughout the experiment.

The sorption-regeneration of fiber 129D (drawn 3:1; 60% SSQ) was studied through 9 cycles in simulated flue gas at 95°C with a flow rate of 121 ml./min. (1592 hr^{-1} space velocity). Data are given in Table XXIII. Figure 6 is the sorption rate curve for the 8th sorption cycle, and Figure 7 shows the overall sorption-regeneration behavior for 9 cycles.

Table XXIII
Sorption-Regeneration of Wet, Simulated Flue Gas on SSQ-Polypropylene Fiber 129 D
(drawn 3:1) (60% SSQ) at 95°C

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
1	0.33	0.0038		
	0.66	0.0076		
	1.00	0.0103**		
		0.0103		
	1.50	0.0132		
	2.00	0.0128		
	2.50	0.0123		
	3.00	0.0114		
	3.50	0.0113		
	4.00	0.0103		
	4.50	0.0110		
	5.00	0.0078		
	5.50	0.0089		
	6.00	0.0098		
	7.17	0.0075		
			1.05***	0.001**
2	0.33	0.0047		
	0.66	0.0071		
	1.00	0.0098**		
		0.0096		
	1.50	0.0082		
	2.00	0.0080		
	2.50	0.0088		
	3.00	0.0087		
	3.50	0.0083		
	4.00	0.0079		
			1.12***	0.0003**
				0.0002

Table XXIII (Cont.)

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
3	0.33	0.0034		
	0.66	0.0065		
	1.00	0.0091**		
		0.0088		
	1.50	0.0078		
	2.00	0.0079		
	2.55	0.0074		
	3.00	0.0079		
	3.50	0.0072		
	4.00	0.0075		
			1.10	0.0004**
				0.0001
4	0.33	0.0039		
	0.66	0.0074		
	1.00	0.0098**		
		0.0088		
	1.50	0.0103		
	2.00	0.0100		
	2.50	0.0100		
	3.00	0.0116		
	3.50	0.0113		
	4.00	0.0103		
	4.50	0.0093		
	4.95	0.0096		
			1.25	+ 0.0002**
				- 0.0002
5	0.33	0.0041		
	0.66	0.0070		
	1.00	0.0088**		
		0.0086		
	1.50	0.0091		
	2.00	0.0088		
	2.50	0.0096		
	3.00	0.0081		
	3.50	0.0094		
	4.00	0.0101		
	4.50	0.0096		
			1.77	0.0008**
				0.0006

Table XXIII (Cont.)

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
6	0.37	0.0033		
	0.66	0.0062		
	1.00	0.0089**		
		0.0081		
	1.50	0.0090		
	2.35	0.0082		
	3.00	0.0079		
	3.50	0.0091		
	4.00	0.0089		
	4.50	0.0099		
	5.64	0.0056		
			1.25	0.0010**
				0.0003
7	0.33	0.0039		
	0.66	0.0067		
	1.00	0.0095**		
		0.0084		
	1.50	0.0087		
	2.00	0.0091		
	2.50	0.0092		
	3.00	0.0095		
	3.50	0.0096		
	4.90	0.0102		
	5.50	0.0117		
	6.00	0.0111		
			2.0	0.0012**
				0.0002
8	0.33	0.0041		
	0.66	0.0067		
	1.00	0.0097**		
		0.0085		
	1.50	0.0085		
	2.00	0.0087		
	3.17	0.0066		
	3.50	0.0087		
	4.00	0.0094		
	4.50	0.0097		
	5.00	0.0101		
	5.50	0.0107		
	6.00	0.0103		
			2.17	0.0015**
				0.0004

Table XXIII (Cont.)

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
9	0.33	0.0037		
	0.66	0.0060		
	1.00	0.0091**		
		0.0076		
	1.50	0.0085		
	2.00	0.0105		
	2.63	0.0099		
	3.13	0.0106		
	3.47	0.0113		
	4.00	0.0099		
	4.50	0.0103		
	5.00	0.0104		
	5.50	0.0102		
			2.17	0.0013** - 0.0002

* g SO_2 + H_2O/g fiber

** Weights based on original starting weight of sample. All other weights are based on the regeneration weight of sample in the preceding cycle.

*** Effluent gas absorbed in standard I_2 solution.

Conditions:

Sorbent: 5.4386 g, drawn (3:1), SSQ-Polypropylene Fiber 129D (60% SSQ)

Sorption:

Feed Gas: Simulated Flue Gas: SO_2 0.31%; NO 0.041%; O_2 2.70%; CO_2 14.00%; H_2O 8.0%; N_2 75.0%, except in the second sorption when the composition was SO_2 0.28%; H_2O 16.0%; and the other gases in proportion.

Flow Rate: 121 ml./min.

Temperature: 95°C

Regeneration:

Feed Gas: dry N_2

Flow Rate: 271 ml./min.

Temperature: 95°C

In Figure 6, the SO_2 feed to the sample is indicated by the broken line. Deviation of the rate curves in these figures from the SO_2 feed line indicates the extent of SO_2 "leakage" through the fiber sample. Rate curves for all cycles are quite similar and indicate that SO_2 removal was complete throughout the first 30-40 minutes. The points on the

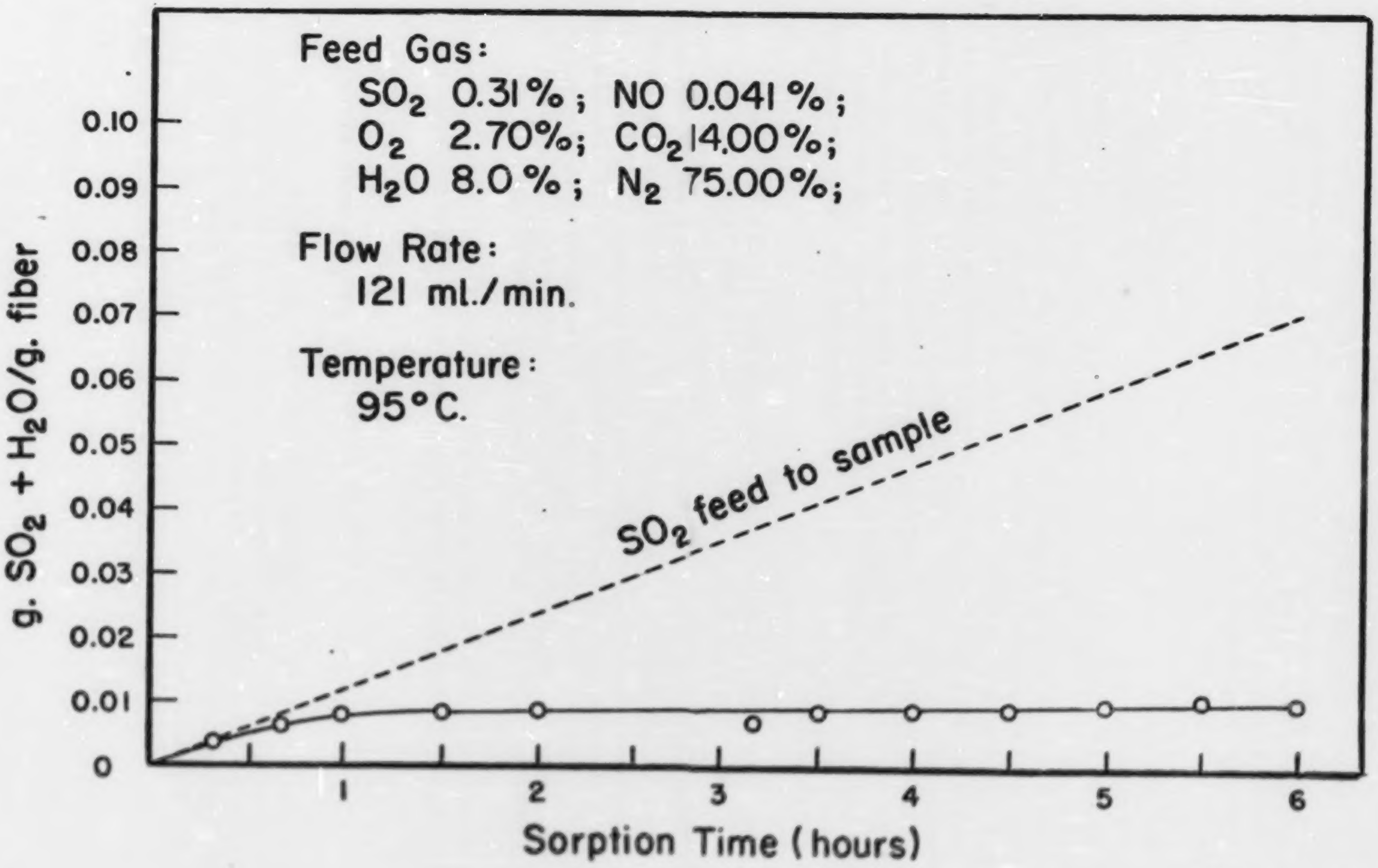


Fig. 6 - Rate of sorption of simulated flue gas on SSQ-polypropylene fiber 129D during the 8th of 9 cycles (drawn 3:1; 60% SSQ).

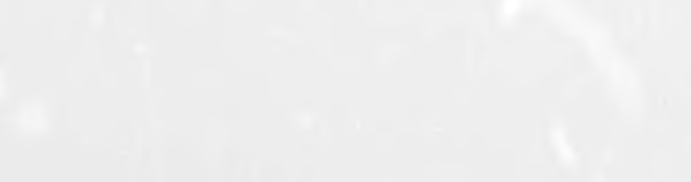
sorption curve in Figure 7 represent a 1 hour sorption time for each cycle. The total sorption time for each cycle, however, was in the range of 4-7 hours, and the cumulative total for all 9 cycles was 47.75 hours. The points on the regeneration curve represent the NTD accumulation for the total sorption time of each cycle. Had the regenerations been carried out at the completion of 1 hour sorption time, the points on the regeneration curve would presumably be appreciably lower, due to a lower NTD accumulation, and would correspond to the "1 hour" points on the sorption curve. Such a graph would show a more correct, and slightly improved regenerability of the fiber. The sorption-regeneration curves in Figure 7 show that although the SO_2 capacity of the fiber at this temperature was rather low in comparison with capacity at 55°C, the capacity was maintained quite well throughout the 9 cycles. This maintenance of capacity was due to the small accumulation of NTD material, as shown by the regeneration curve. The low accumulation of NTD material is in contrast to the considerably greater accumulation occurring during sorption-regeneration cycles at lower temperatures (e.g., 55°C). The probable cause of the low accumulation of NTD material is a reduction in the catalytic effect of H_2O and NO in the oxidation of SO_2 to SO_4, since the concentration of H_2O and presumably NO in the sample is much lower at 95°C than at lower temperatures. Regenerability and NTD accumulation are discussed more fully in section 4.2.

At very high flow rates (space velocities between 99,810 hr^{-1} and 193,381 hr^{-1}) the rate of SO_2 sorption of the 60% SSQ fiber is about 0.047 mg/sec/g fiber in the early stages of the sorption run (less than 1 minute). At these very high flow rates a large amount of SO_2 leakage occurs, since at 99,810 hr^{-1}, for example, SO_2 is fed to the sample at a rate of 3.67 mg/sec/g fiber. The rate of SO_2 removal by the fiber is 0.047 mg/sec/g fiber, hence the SO_2 removal is only a small fraction of the total SO_2 present. At these high flow rates the rate of SO_2 sorption by the fiber is independent of flow rate (see Figure 8). This is to be expected on the basis of the following considerations.

If the reaction at 95°C is considered to be essentially the "dry" reaction, the rate of disappearance of free amine sites should follow the expression:

$$\text{rate} = \frac{-d[\text{amine sites}]}{dt} = k\,[SO_2]\,[\text{amine sites}]$$

If the velocity of feed gas through the bed is high enough so that the SO_2 concentration with time throughout the bed is essentially constant, then the SO_2 concentration term becomes a constant ($C_0 \approx C_n$) and rate = k' [amine sites] Hence, above a certain gas flow rate, the rate of SO_2 sorption by a fiber will be independent of flow rate. At



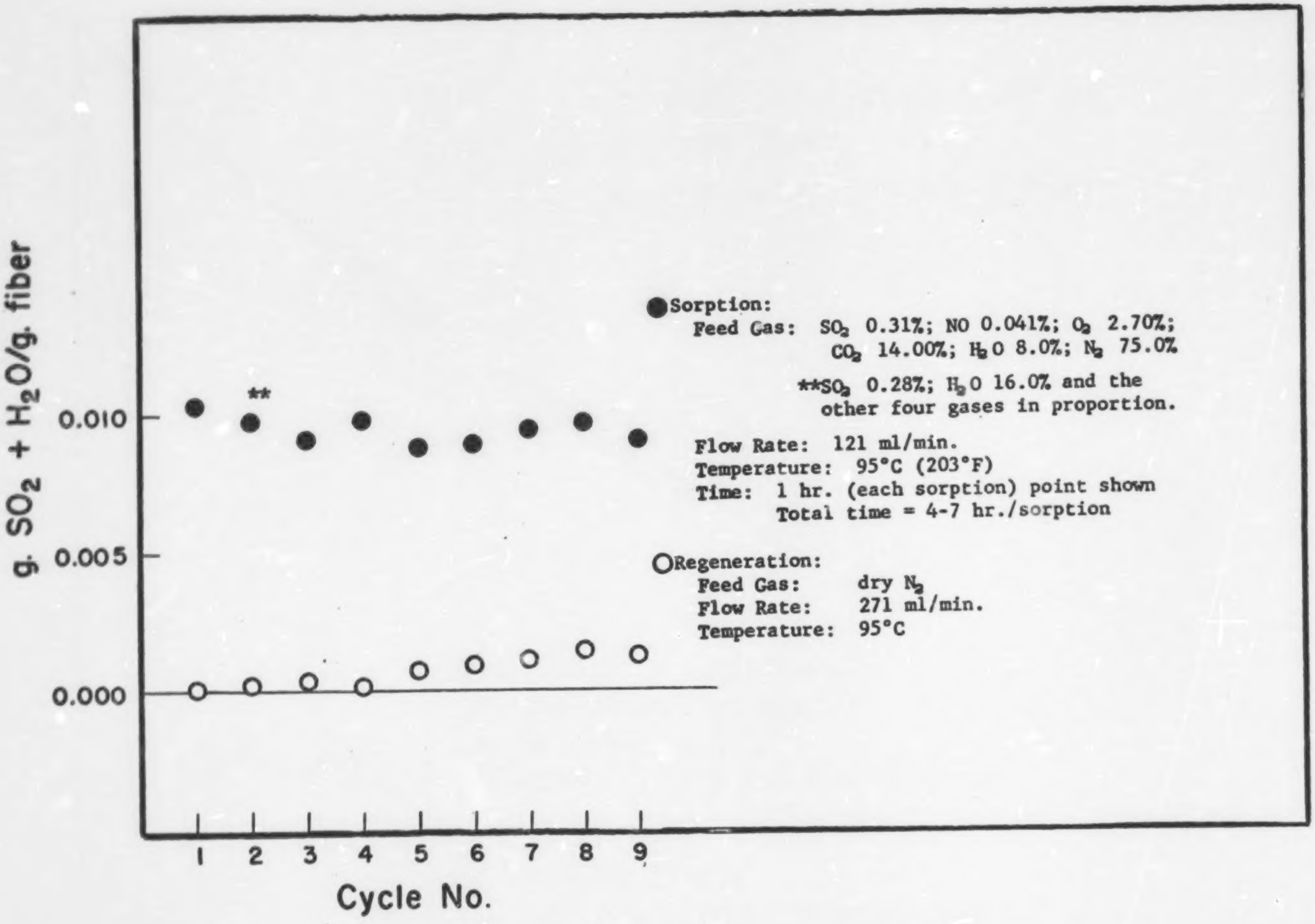


Fig. 7 - Sorption-regeneration of simulated flue gas on SSQ-polypropylene fiber 129D at 95°C at 1 hour sorption time (drawn 3:1; 60% SSQ).

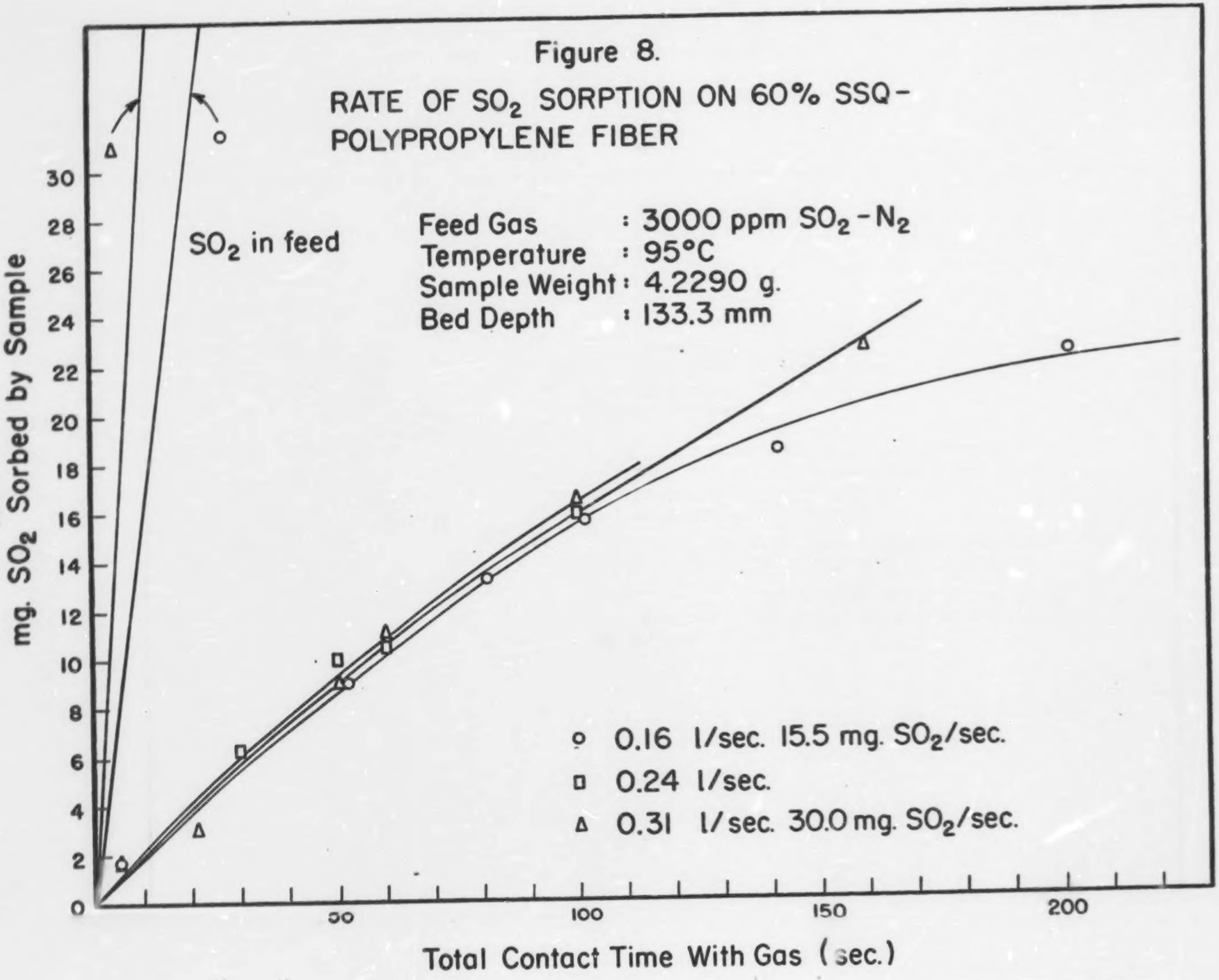


Figure 8.

RATE OF SO_2 SORPTION ON 60% SSQ-POLYPROPYLENE FIBER lower flow rates, where $C_0 > C_1 > C_2 - - - \gg C_n$ the kinetic expression becomes much more complex, and physical factors (bed depth, design of bed, etc.) must be taken into consideration. The experiments at high flow rates were carried out with a dry 3600 ppm SO_2-N_2 mixture, since it was impractical to use simulated flue gas, and it was assumed that the effect of water vapor and other flue gas components are small at this temperature (95°C) and short exposure times.

The rate data discussed above do not allow us to make a satisfactory plant design with quantitative estimates (see section 5.0), but do serve to roughly outline the conditions under which the fibers could be used for SO_2 removal from power plant effluents.

3.11 Alkylated Polyethylenimines

3.11.1 Poly(N-methylethylenimine) (MPEI)

Polyethylenimine (PEI) was screened as a potential sorbent for SO_2. Although its SO_2-sorption capacity was high (61% of the exceptionally high theoretical 1:1 capacity of 1.49 g/g), its stability was unsatisfactory[1]. Polyethylenimine is a highly branched polymer containing primary, secondary, and tertiary amino groups, and since the primary and secondary amine groups can cause undesirable side reactions, and might be responsible for the decomposition observed at elevated temperatures, it seemed advisable to alkylate the imine with a lower-alkyl alkylating agent to convert all primary and secondary amino groups to tertiary amino groups.

Preparation

Two moles (86 g) of PEI (Montrek 12, Dow Chemical Co.) was alkylated with two moles of methyl iodide in a solution of two moles of potassium hydroxide in 1.5 liters of isopropanol at 40-45°C. Carbon, hydrogen, nitrogen and NMR analyses of the yellow, taffy-like product indicated that the extent of methylation was 70-80%.

Evaluation

A sample of poly(N-methylethylenimine) on Chromosorb (16.8% MPEI and 83.2% Chromosorb) was carried through 8 cycles of sorption at 55°C, and regeneration at 110°C with a dry, SO_2-N_2 mixture (5200 ppm SO_2). Figure 9 shows the weight changes on sorption and regeneration for the 8 cycles, based on the original starting weight of the sample (data in Table XXIV).

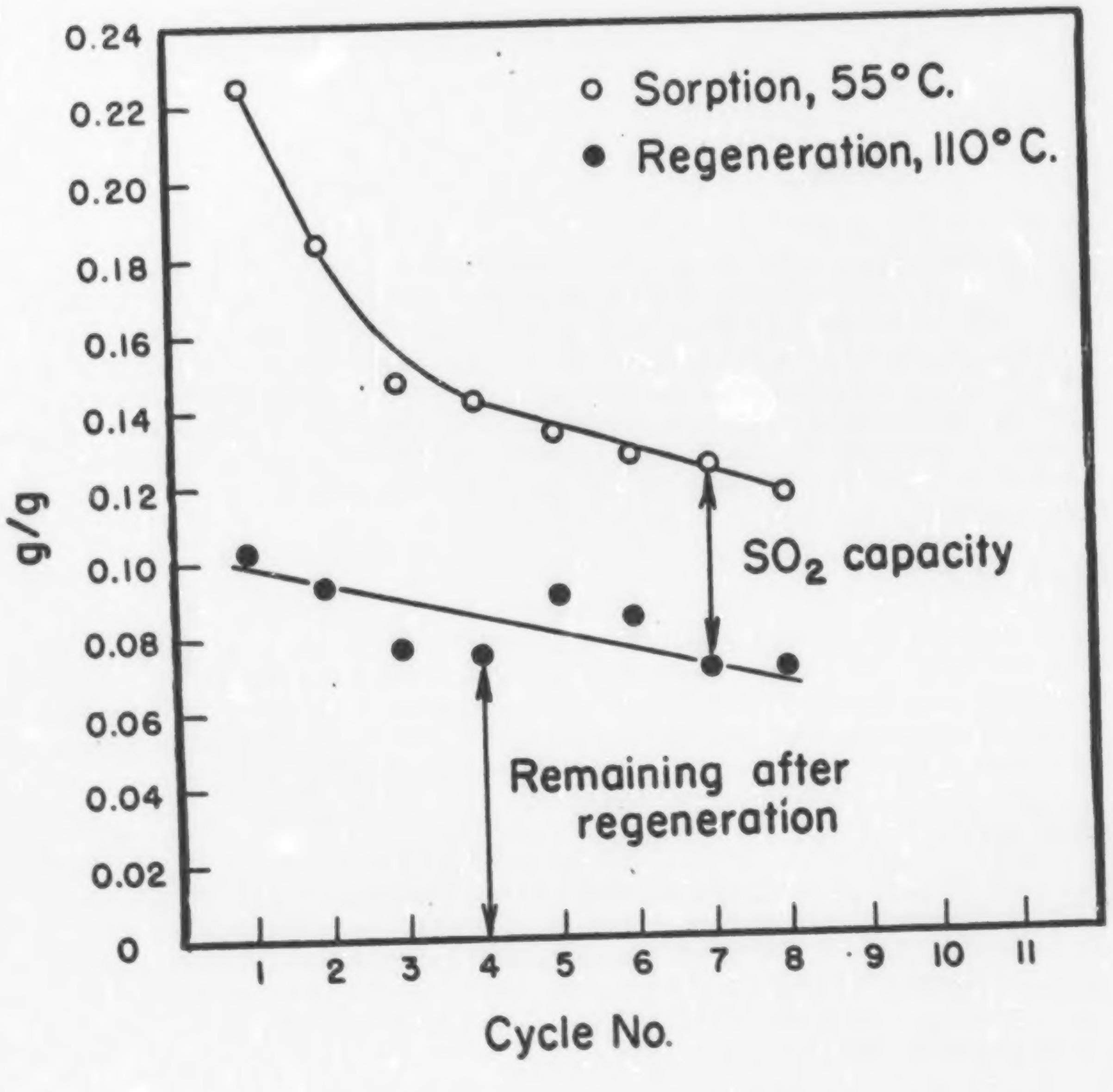


Fig. 9 - Sorption of dry SO_2-N_2 on MPEI

Table XXIV

Sorption-Regeneration Behavior of Poly(N-methylethylenimine)

Cycle No.	Gain g/g*	Remaining After Regeneration, g/g
1	0.2241	0.1022
2	0.1831	0.0933
3	0.1477	0.0773
4	0.1429	0.0758
5	0.1334	0.0900
6	0.1275	0.0844
7	0.1248	0.0698
8	0.1162	0.0707

Conditions:

Sorbent: 2.0029 g mixture of MPEI and Chromosorb W (16.8% of MPEI)

Sorption: Dry 5,260 ppm SO_2-N_2 mixture, 271 ml./min., 55°C

Regeneration: Dry N_2, 271 ml./min., 110°C

*g/g refers to g SO_2/g poly(N-methylethylenimine)

There is a downward trend on both the sorption and regeneration lines. The downward trend on the regeneration line indicates a cumulative weight loss after an initial gain, rather than a gain as would be expected if an "irreversible" sorption of SO_2 occurred. The SO_2 capacity of the sample decreased during the 8 cycles (0.0237 g/g on the 3rd cycle to 0.0153 g/g on the 8th cycle).

The rather steep negative slope of both the sorption and regeneration lines indicates that the sample suffered a cumulative weight loss during the 8 cycles after initial irreversible sorption of SO_2 (see section 4.2.1). The most plausible explanation for this is that the whole sample, or some component of it, was sufficiently volatile to be slowly vaporized under the sorption-regeneration conditions used. Since the sorbent was methylated Montrek 12, it would undoubtedly be less volatile and probably more thermally stable than Montrek 12 itself. And in view of the stability of Montrek 12 during thermogravimetric analysis, (stable to > 200°C in air, stable to > 250°C in nitrogen), this result is probably not due to direct thermal instability, but is more probably due to a decomposition by reaction with SO_2.

Table XXV

Sorption-Regeneration Behavior of Poly(N-phenethylethylenimine)

Cycle No.	Gain During Sorption, g/g* imine	Remaining After Regeneration, g/g* imine
1	0.2112	0.0204
2	0.2005	0.0247
3	0.1908	0.0468
4	0.1871	0.0355
5	0.1736	0.0323
6	0.1613	0.0543
7	0.1553	0.0538
8	0.1672	0.0554
9	0.1446	0.0591

Conditions: 1.1127 g mixture of 16.72% poly(N-phenethylethylenimine) and 83.28% Chromosorb W

Sorption: SO_2 5,260 ppm

H_2O 8.0%

N_2 balance

Theoretical capacity, 0.4352 g SO_2/g imine

Flow Rate: 271 ml./min., 55°C

Regeneration: Dry N_2, 271 ml./min. 95°C

*g/g represents g SO_2 + H_2O/g poly(N-phenethylethylenimine)

3.11.2 Poly(N-phenethylethylenimine)

A research sample of poly(N-phenethylethylenimine) was obtained from the Dow Company. An evaluation of this material as a 16.72% mixture with Chromosorb W, through 9 sorption-regeneration cycles was made. Sorptions were at 55°C in a mixture of 5,260 ppm. SO_2, nitrogen and 8% water vapor. Regenerations were at 95°C in dry nitrogen. Figure 10 shows the weight changes on a g SO_2/g sorbent in original sample basis, during the 9 cycles. (Data in Table XXV).

There is a downward trend on the sorption line and an upward trend on the regeneration line. This is an example in which there occurs a simultaneous, cumulative, loss of SO_2 capacity and an "irreversible" sorption. These experimental data show that poly(N-phenethylethylenimine) has a short life - perhaps no more than 14 cycles of sorption-regeneration - as an effective sorbent for sulfur dioxide.

Following the final (9th) regeneration, the sample [16.72% poly-(phenethylethylenimine)] was analyzed for nitrogen and sulfur. Cal-

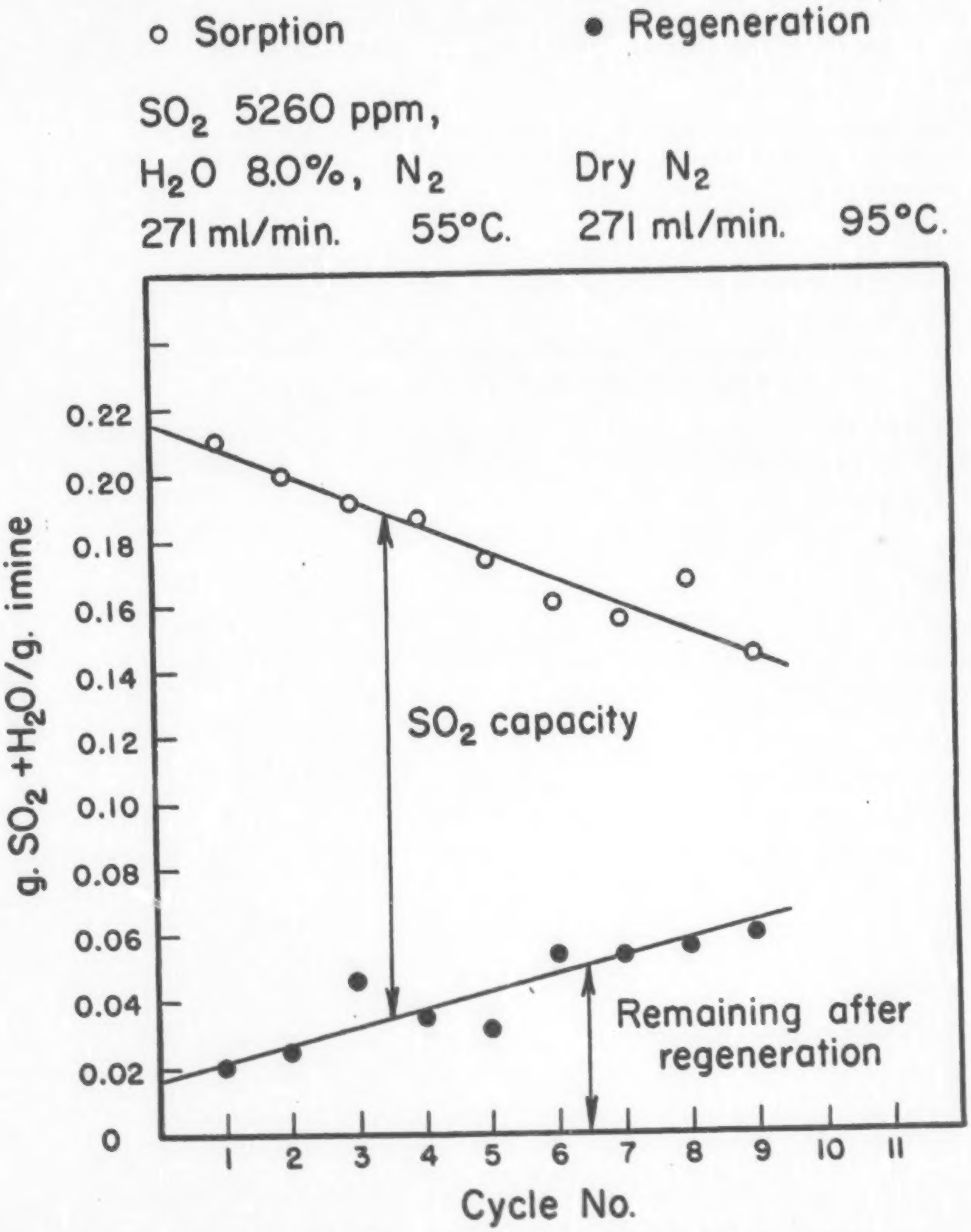


Fig. 10 - Sorption-regeneration of SO_2-H_2O-N_2 gas on poly(N-phenethylethylenimine) 16.72% on Chromosorb W

culated: %N, 1.59; % S, 0.00; Found: %N, 1.51; % S, 0.515. The sulfur content indicates that a significant amount of some sulfur-containing material was "irreversibly" sorbed on the poly(N-phenethylethylenimine). A calculation shows that this residual sulfur corresponds to 20% of the sulfur in a 1:1 complex of the imine and sulfur dioxide.

A thermogravimetric analysis was carried out on poly(N-phenethylethylenimine) (Table XXVI). The data indicate that the polymer probably has sufficient thermal stability to withstand melt-spinning with polypropylene, and that the observed decomposition in SO_2 sorption-regeneration cycling is not due to thermal effects alone.

Table XXVI

Thermogravimetric Analysis of Poly(N-phenethylethylenimine)

Temperature Range (°C)	Temperature Increase (°C)	Weight Loss (%)	Cumulative Weight loss (%)
30-250	220	2	2
250-370	120	74	76
370-500	130	6	82
500-600	100	12	94
600-700	100	1	95

4.0 REGENERATION

In any sorption process for removing SO_2 from waste gases it is highly desirable that the process be regenerative. This is particularly true for treating power plant effluents because of the enormous quantities of SO_2 which must be handled. Even the use of very inexpensive sorbents, if not regenerable, will lead to high costs because of transportation and disposal requirements.

In cases where the sorbent material has significant cost, a long service life (high degree of regenerability) is an absolute necessity for economic feasibility.

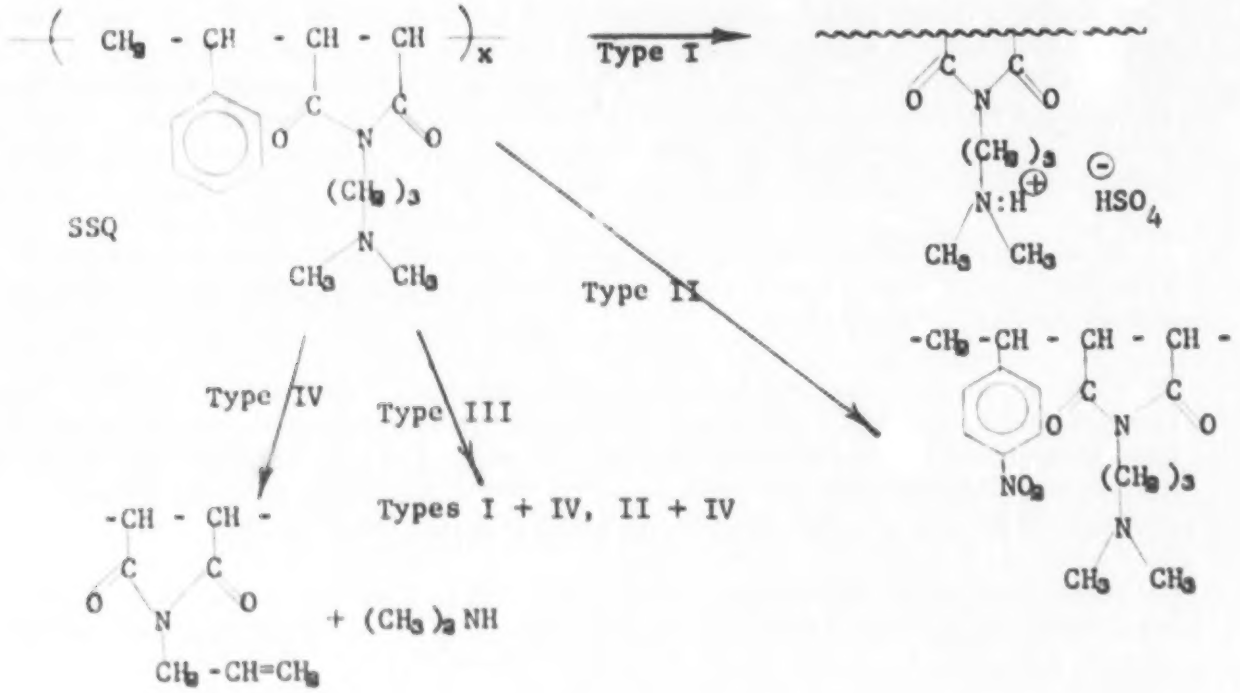
In view of this, regenerability of our sorbent fibers was studied in considerable detail. We carried fiber samples through multiple sorption-regeneration cycles to determine what changes in rate and capacity occurred, and to seek evidence of irreversible chemical reactions between the sorbent and SO_2 or other flue gas components.

Section 3.7 deals with the mechanism of sorption of reversibly bound SO_2; section 4.2 is primarily concerned with the chemistry and mechanism of formation of non-thermally desorbable materials.

From work reported earlier[1] under this contract, it is known that SO_2 sorbed by SSQ can be desorbed by increasing the temperature of the sample and flushing with inert gas; however, there were indications that a loss of capacity occurred with succeeding cycles. In order to investigate the nature of the processes involved and to find means of dealing with the loss of capacity, either by preventing the undesirable side reactions or by devising a chemical treatment which could be applied to the fiber, four possible types of sorption-regeneration behavior were envisioned:

Type I	Irreversible sorption with loss of SO_2 capacity
Type II	Irreversible sorption without loss of SO_2 capacity
Type III	Loss of SO_2 capacity without irreversible sorption
Type IV	Loss of SO_2 capacity with loss of weight

Examples of processes which could lead to each type of behavior are illustrated below:



Type I behavior is expected for a situation where an acidic species is present which forms a more stable adduct with the amine nitrogen than SO_2 does, and ties up sorption sites. Such species could be SO_3, H_2SO_4, HNO_3, etc. In cases such as this, the type of sorption-regeneration graph shown in Figure 11a is expected. The relative slopes of the two lines depend upon the equivalent weight of the irreversibly sorbed species. On a mole SO_2/equivalent SSQ the curve would be as shown in Figure 11b where each mole/equivalent SO_2 capacity lost would correspond to each mole/equivalent of material permanently sorbed.

Type II behavior is expected from the accumulation of a material which does not tie up amine nitrogen. Possibilities include reaction with centers other than the amine nitrogen (e.g. nitration or sulfonation of the aromatic ring) or deposition of a solid in the sorbent bed.

In the consideration of a Type III situation, it is difficult to envision a chemical process whereby amine nitrogen can be deactivated toward SO_2, without a net weight gain. Possibilities include, however: a) a molecular rearrangement of the sorbent, b) the occurrence of simultaneous processes, one leading to a weight gain and one leading to a weight loss, c) a physical change, such as slow crystallization of the polymer, leading to a decrease in the number of physically available sites.

Type IV behavior is expected where a decomposition of the polymer, such as loss of amino groups through pyrolysis, occurs. Loss of sample

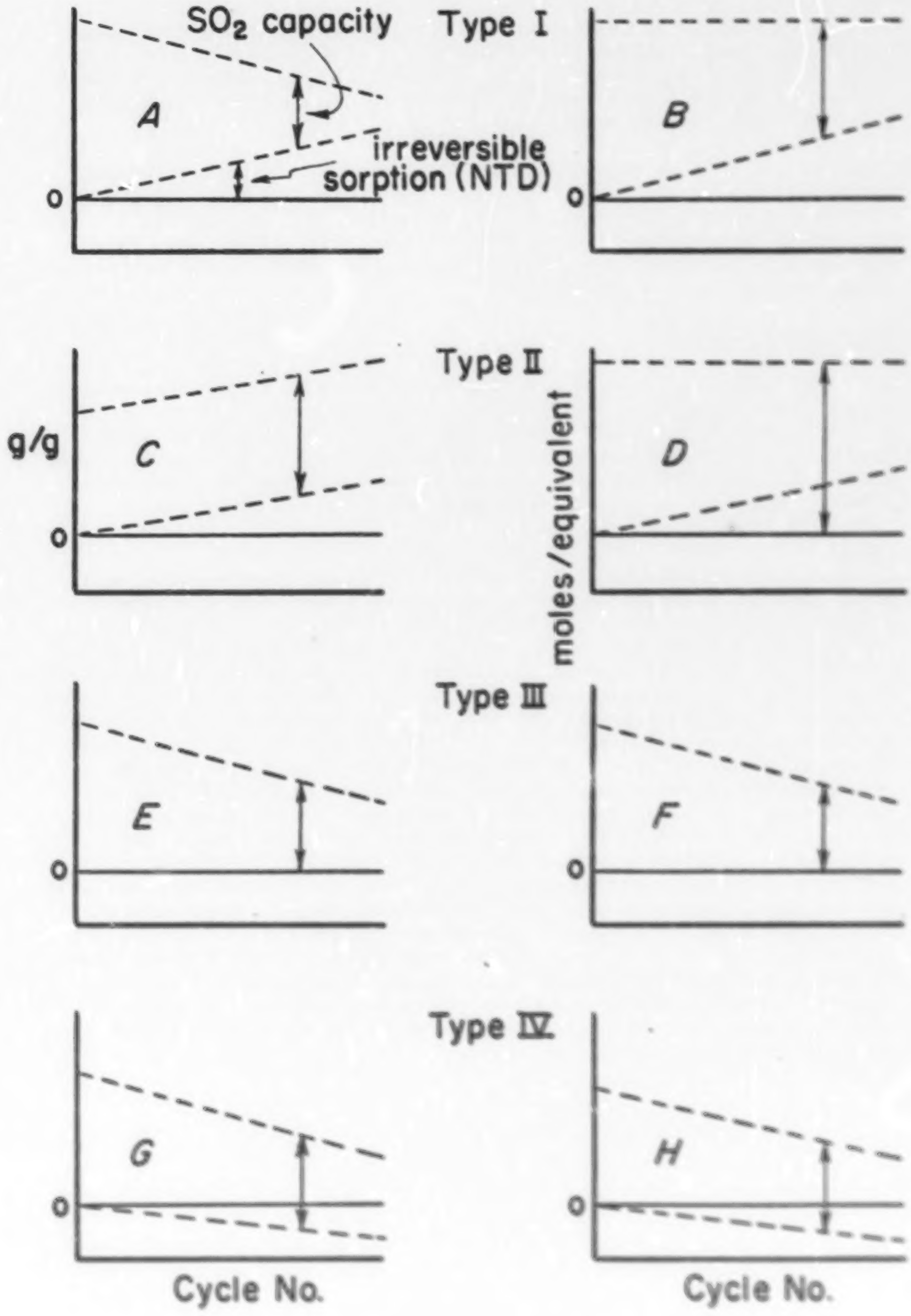

SO$_2$ capacity
Type I
A
irreversible sorption (NTD)
0
B
0
Type II
g/g
C
0
D
moles/equivalent
Type III
E
0
F
0
Type IV
G
0
H
0
Cycle No.
Cycle No.

Fig. 11 - Sorption-regeneration curves for various process types

itself, as dust or through volatilization, would be easily detected, since large sample weight loss would be required to result in a relatively small SO_2 capacity loss, e.g., if the SO_2 capacity of the sorbent is say, 20% by weight, a 10% loss in SO_2 capacity (0.02 g/g) requires a 10% loss in sample weight (0.1 g).

When carried through repeated sorption-regeneration cycles with simulated flue gas at 55°C, both polypropylene-SSQ fibers and pure SSQ show Type I behavior, indicating the formation of a non-thermally desorbable (NTD) adduct or salt with the amino groups of SSQ. This NTD has been identified as sulfate, presumably formed by the oxidation of SO_2 during the process.

4.1 Regeneration Methods

Two driving forces for desorbing SO_2 from the fiber by physical means are: 1) increaseing the temperature of the fiber, and 2) removing the SO_2 from the gas phase surrounding the fiber. For maximum rate and completeness of regeneration a combination of both is desirable. Three methods for removing SO_2 from the environment of a heated fiber were investigated: vacuum, superheated steam and an inert sweep gas.

4.1.1 Vacuum

During two SO_2 sorption-regeneration cycles of simulated flue gas on polypropylene-SSQ fiber 129D (60% SSQ, drawn 3:1), the regenerations were accomplished by applying vacuum to the fiber sample for a one hour period at 125°C. The pressure on the sample during these regenerations by vacuum was 40 mm (Hg). Data are given in Table XXVII and Figure 12. Comparative data on regenerations by steam and nitrogen, and by nitrogen only are also shown in Figure 12. The reason for the final weight of the sample being less than the original starting weight (before sorption) may possibly have been due to a slight mechanical loss of sample caused by a rapid shifting of the sample in the sample holder during pressure changes when vacuum was applied or released. This effect was not apparent during the second regeneration. Since only two regenerations by vacuum were carried out, the minimum time required for complete regeneration was not established, but the data suggest that this minimum time might be somewhere between 0.5 to 1 hours. In comparison with the results obtained from regenerations by steam (see following paragraph) regeneration by vacuum is apparently a slower process. Although the economics of regeneration by vacuum are probably less promising than steam or sweep gas, the experimental data indicate that the method is workable.

Table XXVII

Sorption-Regeneration of Simulated Flue Gas on Polypropylene-SSQ Fiber 129D

(drawn 3:1) (60% SSQ)

Experiment A

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Method of Regeneration	Regeneration Time (hrs.)	Remaining After Regeneration (g/g fiber)
1	1.0	0.0053			
			Vacuum	0.5	-0.0013
				1.0	-0.0036
2	2.0	0.0072			
			Vacuum	1.0	0.0002
3	4.16	0.0071			
			Steam	0.16	
			N_2	0.5	0.0045

* g SO_2 + H_2O/g fiber

Conditions:

Sorbent: 4.2570 g SSQ-Polypropylene Fiber 129D (drawn 3:1) (60% SSQ)

Sorption:

Feed Gas: SO_2 0.31%; NO 0.041%; O_2 2.70%; CO_2 14.00%; H_2O 8.0%; N_2 75.0%

Flow Rate: 121 ml./min.

Temperature: 95°C

Regeneration:

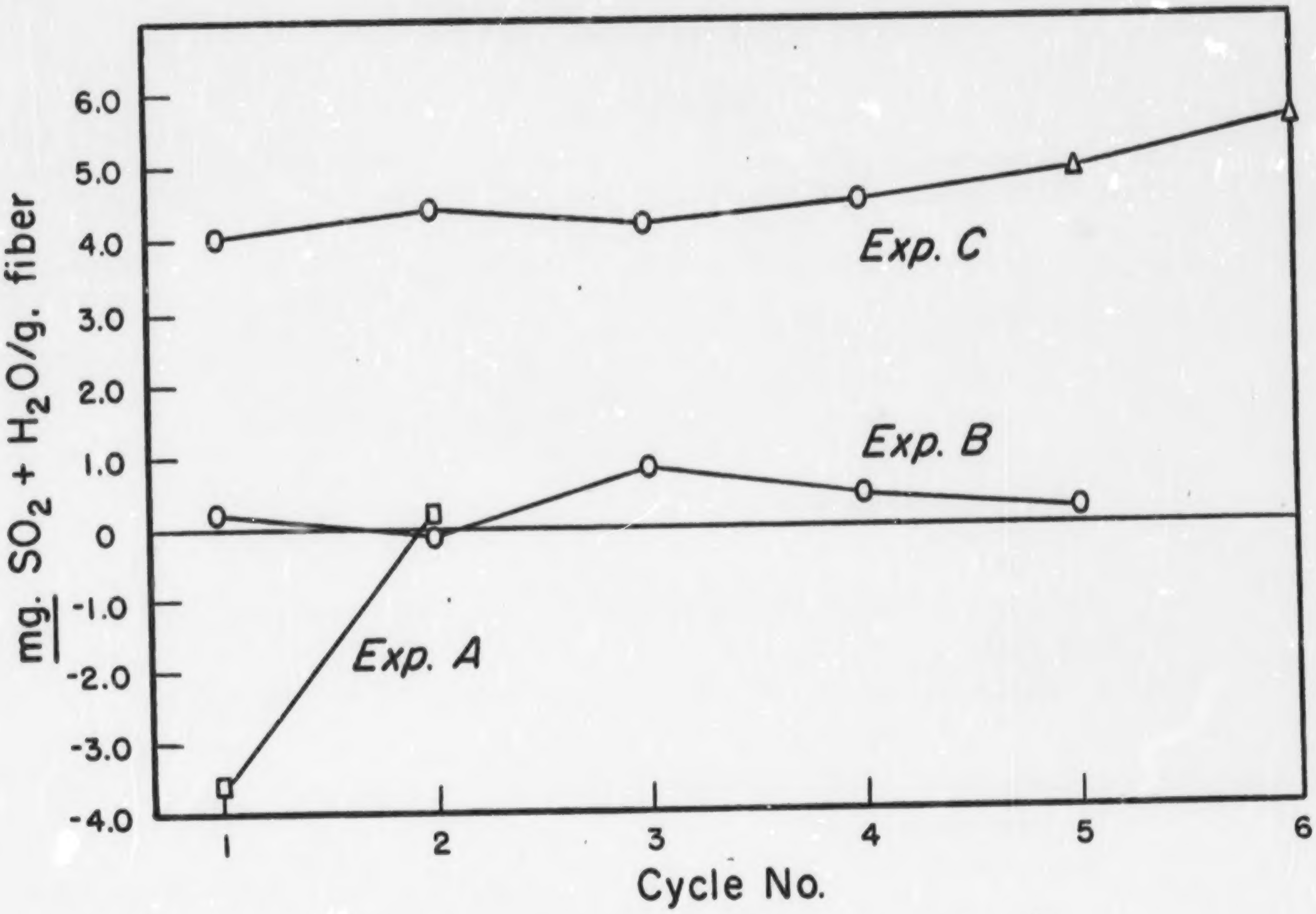
Flow Rate: Steam 1341 ml./min.; N_2 271 ml./min.

Temperature: 125°C

Pressure During Vacuum Regeneration: 40 mm. Hg.

4.1.2 Steam

During ten SO_2 sorption-regeneration cycles of simulated flue gas on polypropylene-SSQ fiber 129D (60% SSQ, drawn 3:1), the regenerations were accomplished by passing superheated steam (125°C) through the fiber sample for a period of 10 minutes, followed by flushing with dry nitrogen at 125°C for 15 minutes. The flow rates of steam and nitrogen were 1,341 ml./min. and 271 ml./min. respectively. Data are given in Tables XXVII, XXVIII and XXIX. The flushing with nitrogen was used to remove water vapor sorbed by the sample from the steam. This sorption of water vapor by the sample during steam regeneration was indicated by the increase in weight of the sample - an average of 2.3 mg. for each regeneration.



	□	○	△
Method	Vacuum	Steam	N_2
Time (min.)	60	Steam for 10 min., then N_2 for 15 min.	120
Temp. (°C)	125	125 (superheated steam)	95
Flow Rate	-	Steam 1371 ml/min. N_2 271 ml/min.	271 ml/min.
Pressure	40 mm Hg	1 atm	1 atm

Fig. 12 - Regeneration, by various methods, of SSQ-polypropylene fiber 129D (drawn 3:1, 60% SSQ) after sorption (to saturation) of simulated flue gas

Table XXVIII

Sorption-Regeneration of Simulated Flue Gas on SSQ-Polypropylene Fiber 129D

(drawn 3:1) (60% SSQ)

Experiment B

Cycle No.	Sorption Time (hrs.)	Gain During Sorption (g/g)*	Regeneration Time (min.)	Remaining After Regeneration (g/g fiber)	Volume of H_2O Effluent (ml.)
1	1.5	0.0056			
			Steam 10	0.0060	
			N_2 15	0.0002	
2	1.0	0.0049			
			Steam 10	0.0083	
			N_2 15	-0.0001	
3	1.5	0.0062			
			Steam 10	0.0053	6.4
			N_2 15	0.0008	
4	1.5	0.0049			
	2.5	0.0070			
			Steam 10	0.0084	8.5
			N_2 15	0.0004	
5	2.66	0.0059			
			Steam 10	0.0082	**
			N_2 15	0.0002	

* g SO_2 + H_2O/g fiber

** Effluent collected in standardized iodine solution

Conditions:

Sorbent: 4.2868 g SSQ-Polypropylene Fiber 129D (drawn 3:1) (60% SSQ)

Sorption:

Feed Gas: SO_2 0.31%; NO 0.041%; O_2 2.70%; CO_2 14.0%; H_2O 8.0%; N_2 75.0%

Flow Rate: 121 ml./min.

Temperature: 95°C

Regeneration:

Flow Rate: Steam 1341 ml./min.; N_2 271 ml./min.

Temperature: 125°C

Table XXIX

Sorption-Regeneration of Simulated Flue Gas on SSQ-Polypropylene Fiber 129D

(60% SSQ) drawn 3:1)

Experiment C

Cycle No.	Temp. °C	Sorption Time (Hrs.)	Gain During Sorption (g/g)*	Regeneration Time (min.)	Remaining After Regeneration (g/g fiber)	Volume of H_2O Effluent (ml.)
1	55	2.5	0.0336			
				Steam 10	0.0128	7.9
				N_2 15	0.0040	
2	55	2.5	0.0340			
				Steam 10	0.0129	7.6
				N_2 15	0.0044	
3	95	2.5	0.0107			
				Steam 10	0.0154	6.8
				N_2 15	0.0042	
4	95	3.25	0.0112			
				Steam 10	0.0140	7.2
				N_2 15	0.0045	
5	95	2.0	0.0109			
				N_2 113	0.0049	
6	95	2.0	0.0111			
				N_2 120	0.0056	

* g SO_2 + H_2O/g fiber

Conditions:

Sorbent: 3.9828 g SSQ-Polypropylene Fiber 129D (Drawn 3:1) (60% SSQ)

Sorption:

Feed Gas: SO_2 0.31%; NO 0.041%; O_2 2.70%; CO_2 14.0%; H_2O 8.0%; N_2 75.0%

Flow Rate: 121 ml./min.

Temperature: Cycles 1-2 55°C; Cycles 3-6 95°C

Regeneration:

Flow Rate: Steam 1341 ml./min.; N_2 271 ml./min.

Temperature: Steam 125°C; N_2 95°C

Since the duration of each steam regeneration was 10 minutes, the minimum time required for complete regeneration was not established, but the data indicate that it would be less than 10 minutes.

The apparent presence of non-desorbable material in the sample resulted in a regeneration line at a 3.5 - 5.5 mg. higher level than for the vacuum regeneration (see Figure 12). This is attributed to the fact that the first two sorptions were carried out at 55°C, at which temperature non-desorbable material has been found to accumulate in a fiber sample much more rapidly than at temperatures of 95°C or higher. This NTD material, which formed in the fiber sample during the first and second sorptions (at 55°C), could not be desorbed either by steam or nitrogen, and remained on the sample thoughout the experiment.

Although the economic aspects of regeneration by steam have not been thoroughly determined as yet, the experimental data indicate that the method is rapid, efficient and the most likely to be economically sound. It has an added advantage over regeneration either by vacuum or a sweep-gas in that condensation of the effluent yields highly concentrated SO_2 and a relatively small amount of an aqueous solution of SO_2.

4.1.3 Sweep Gas

Regeneration by using nitrogen as a sweep gas has been found to be effective over a wide range of temperature but it does not give a satisfactory concentration of SO_2 in the effluent gas.

4.2 Non-Thermally Desorbable (NTD) Materials

4.2.1 NTD Formation - Causes

Samples of granular SSQ were treated with dry simulated flue gas, dry simulated flue gas minus NO, dry SO_2-N_2, wet SO_2-N_2, and wet simulated flue gas. The table below illustrates qualitatively the effect upon NTD accumulation at 55°C.

Gas Mixture	NTD Accumulation
SO_2-N_2	Very slight
SO_2-CO_2-O_2-NO-N_2	Moderate
SO_2-CO_2-O_2-N_2	Very slight
SO_2-H_2O-N_2	Slight
SO_2-CO_2-O_2-NO-H_2O-N_2	Heavy

SO_2-N_2

A sample of dry SSQ carried through 25 cycles of sorption and regeneration with a dry 5200 ppm/SO_2-N_2 mixture at 55°C shows no cumulative weight gain (Table XXX, Figure 13). There is a slight weight loss over the series (6.5mg, 0.67% on the weight of the sample) but it is probably not significant, since it has not been observed in other similar experiments. The SO_2 capacity of the sample remained relatively constant (0.1325 g/g initially to 0.1275 g/g at 25 cycles). Under these conditions, therefore, indications are that very little irreversible side reaction is occurring.

SO_2-CO_2-O_2-NO-N_2

A similar series, run with a dry simulated flue gas shows a cumulative weight gain of 0.035 g/g over 25 cycles, indicating irreversible sorption of some material from the gas mixture. The SO_2 capacity was reduced from 0.122 g/g to 0.082 g/g (Figure 14, Table XXXI).

SO_2-CO_2-O_2-N_2

A third series, run with a simulated flue gas but without NO present, does not show irreversible sorption over 14 cycles, and appears similar to the SO_2-N_2 case. (Figure 15, Table XXXII) On the basis of this data it appears that in a dry system NO is responsible for the production of NTD. It is likely that a series of reactions similar to the chamber process is occurring:

$$\begin{aligned} NO + O_2 &\longrightarrow NO_2 \\ NO_2 + SO_2 &\longrightarrow SO_3 + NO \\ SO_3 + H_2O &\longrightarrow H_2SO_4 \end{aligned}$$

Since it is known that NO, NO_2, and SO_2 all form complexes with amines, it is possible that the sorbent facilitates this process by holding one or more of the components "in place", thereby increasing the effective concentration of NO and NO_2, e.g.:

$$\begin{aligned} {>}N{:}NO + O_2 &\longrightarrow {>}N{:}NO_2 \\ {>}N{:}NO_2 + SO_2 &\longrightarrow {>}N{:}SO_3 + {>}N{:}NO \\ {>}N{:}SO_3 + H_2O &\longrightarrow {>}NH^{+}\ HSO_4 \end{aligned}$$

These results also indicate that O_2 and CO_2, at the levels present in flue gas, do not in themselves lead to NTD formation or degradation of the sorbent in a dry system.

TABLE XXX

Sorption-Regeneration of SO_2-N_2 on Dry SSQ

Cycle No.	Gain, g/g	Remaining After Regeneration, g/g
2	0.1324	0.0000
3	0.1334	+0.0006
4	0.1362	+0.0001
5	0.1334	0.0000
6	0.1286	-0.0029
7	0.1251	-0.0040
8	0.1251	-0.0034
9	0.1258	-0.0030
10	0.1212	-0.0049
11	0.1206	-0.0045
12	0.1228	-0.0048
13	0.1250	-0.0040
14	0.1235	-0.0046
15	0.1223	-0.0051
16	0.1206	-0.0055
17	0.1234	-0.0047
18	0.1208	-0.0042
19	0.1274	-0.0039
20	0.1205	-0.0072
21	0.1216	-0.0072
22	0.1184	-0.0069
23	0.1191	-0.0035
24	0.1215	-0.0063
25	0.1210	-0.0065

Conditions: 0.9741 g bed dry SSQ

Sorption: dry 5260 ppm SO_2-N_2 mixture, 271 ml./min., 55°C

Regeneration: dry N_2, 271 ml./min., 95°C

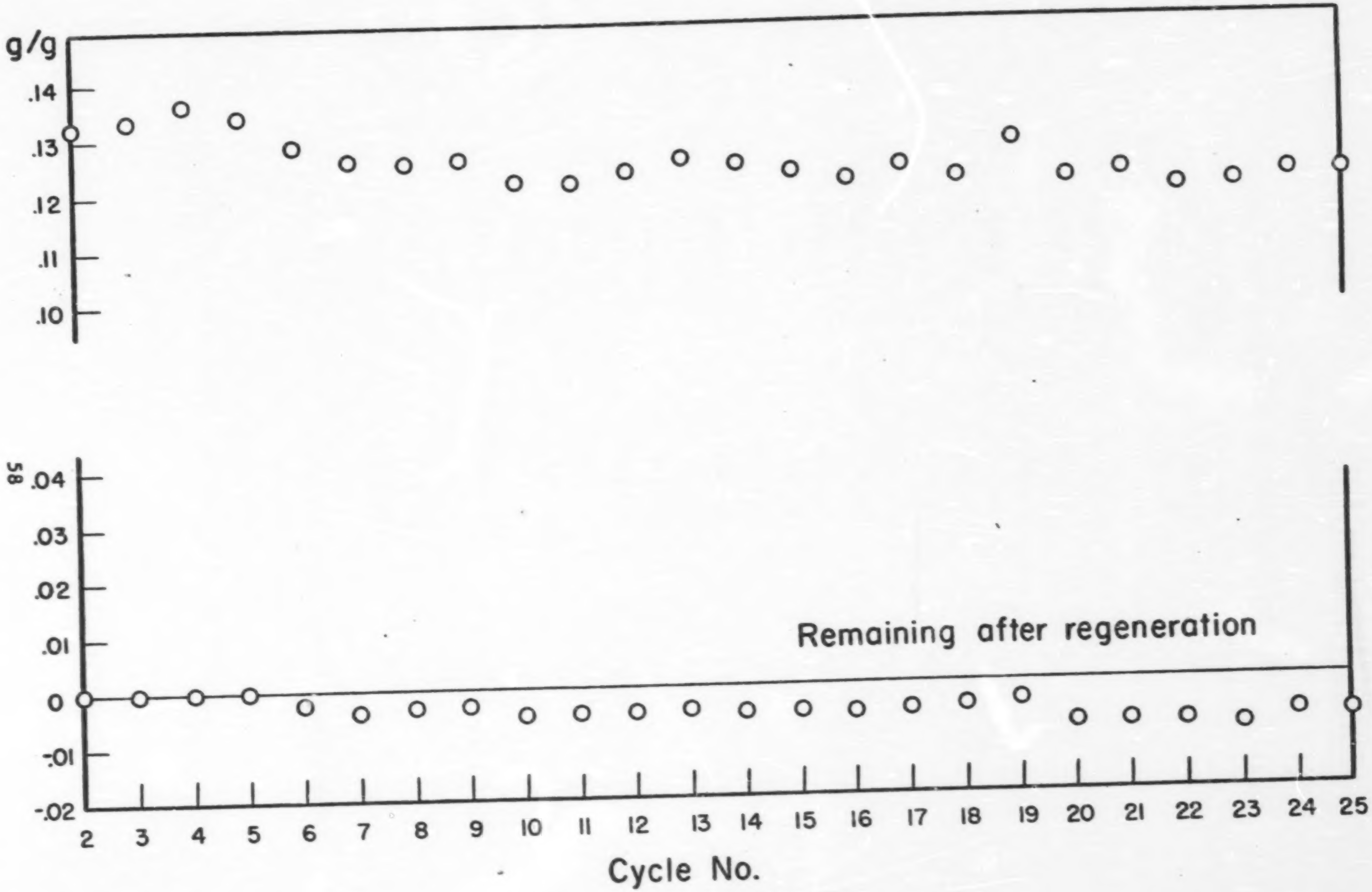


Fig. 13 - Dry SO_2-N_2 on SSQ

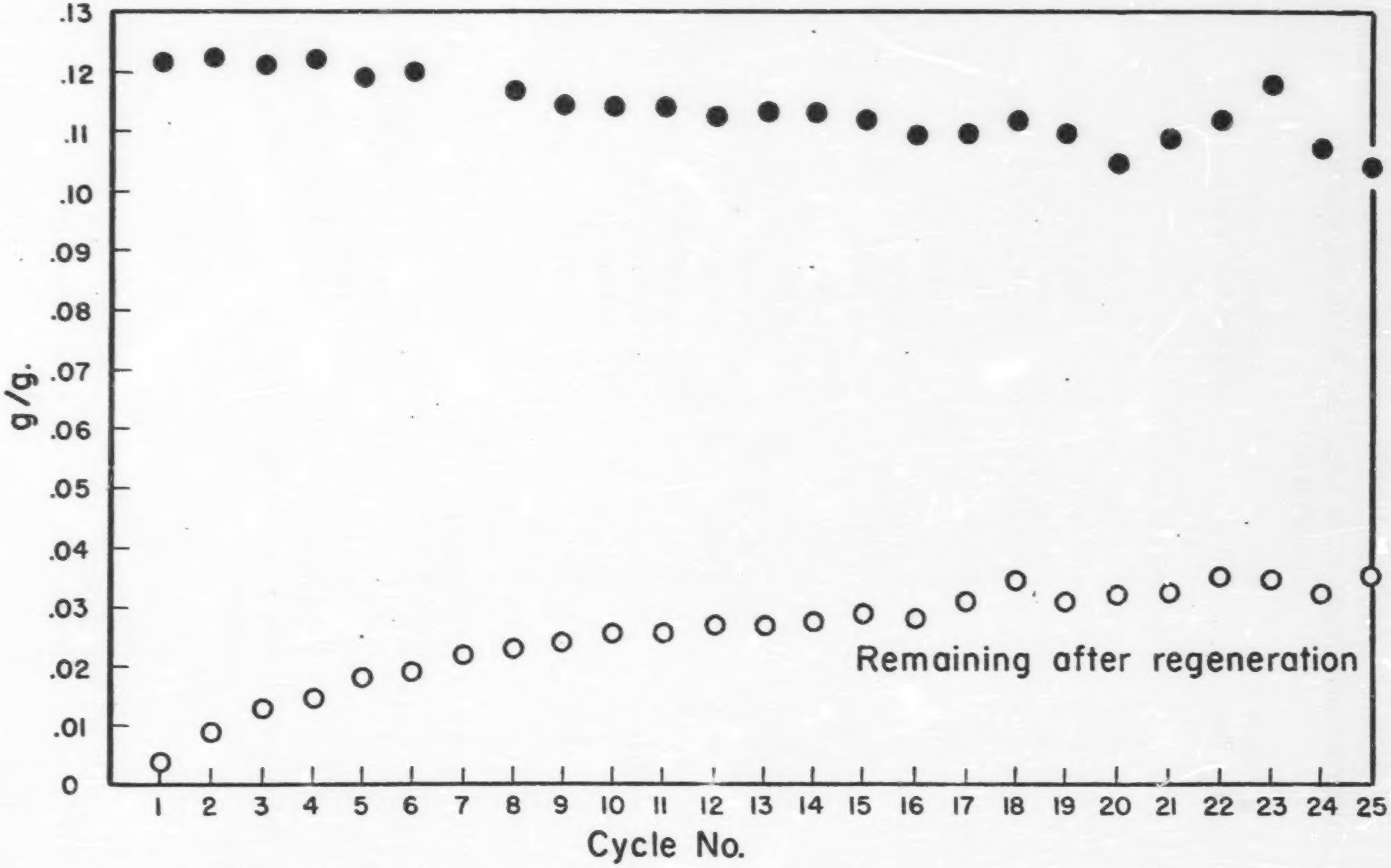


Fig. 14 - Dry SO_2-CO_2-O_2-NO-N_2 on SSQ

Table XXXI

Sorption-Regeneration of SO_2 - CO_2 - O_2 NO- N_2 on Dry SSQ

Experiment B

Cycle No.	Gain, g/g	Remaining After Regeneration, g/g
1	0.1215	+0.0035
2	0.1223	0.0091
3	0.1205	0.0131
4	0.1216	0.0147
5	0.1190	0.0185
6	0.1200	0.0190
7	0.1132	0.0221
8	0.1165	0.0230
9	0.1145	0.0245
10	0.1141	0.0257
11	0.1140	0.0255
12	0.1135	0.0270
13	0.1130	0.0265
14	0.1131	0.0275
15	0.1113	0.0285
16	0.1090	0.0281
17	0.1095	0.0305
18	0.1114	0.0344
19	0.1096	0.0308
20	0.1045	0.0320
21	0.1085	0.0324
22	0.1115	0.0348
23	0.1174	0.0345
24	0.1070	0.0327
25	0.1035	0.0350

Conditions: 0.9730 g bed dry SSQ

Sorption: dry mixture

SO_2	0.34%
CO_2	15.2
O_2	2.94
NO	0.048
N_2	81.47

271 ml./min., 55°C

Regeneration: dry N_2, 271 ml./min., 95°C

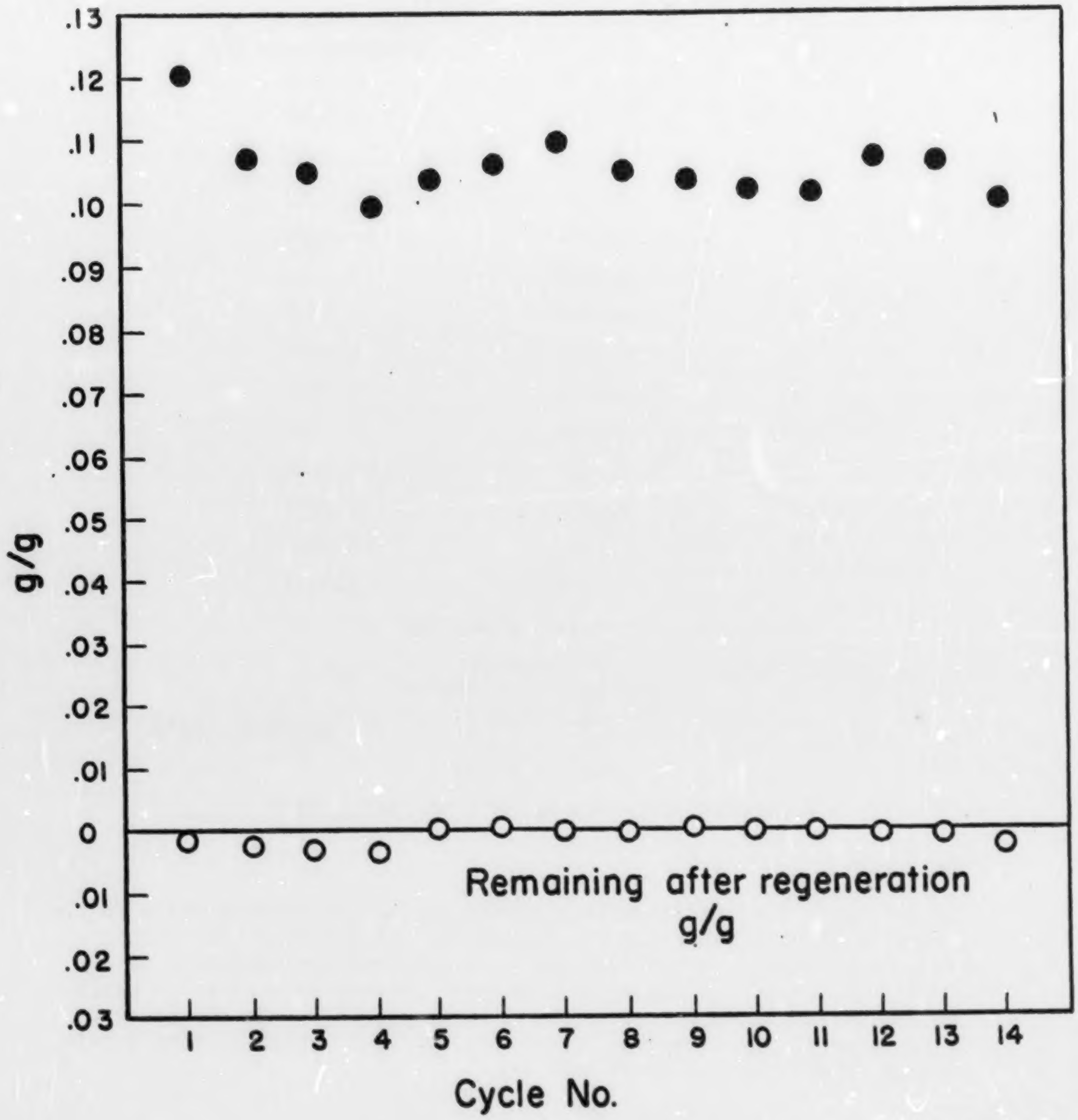


Fig. 15 - Dry SO_2-CO_2-O_2-N_2 on SSQ

Table XXXII

Sorption-Regeneration of SO_2 - CO_2 - O_2 - N_2 on Dry SSQ

Experiment C

Cycle No.	Gain g/g	Remaining After Regeneration, g/g
1	0.1204	-0.0020
2	0.1171	-0.0027
3	0.1149	-0.0032
4	0.1094	-0.0038
5	0.1138	+0.0003
6	0.1168	-0.0003
7	0.1200	+0.0005
8	0.1151	-0.0007
9	0.1139	-0.0001
10	0.1122	+0.0004
11	0.1121	-0.0006
12	0.1176	+0.0015
13	0.1168	-0.0012
14	0.1102	-0.0037

Conditions: 0.9534 g dry SSQ

Sorption: dry mixture, 271 ml./min., 55°C

SO_2	0.34%	
CO_2	15.2	271 ml./min., 55°C
O_2	2.94	
N_2	81.52	

Regeneration: dry N_2, 271 ml./min., 95°C

SO_2-H_2O-N_2

The presence of water vapor in a simple SO_2-N_2 gas mixture leads to the formation of NTD, Table XXXIII, Figure 16. Although in this system there is no oxygen in the feed gas to accomplish the oxidation of SO_2 to sulfate, traces of atmospheric oxygen, introduced during the weighing and regeneration processes could be responsible. In the presence of water vapor SO_2 is sorbed largely as bisulfite which is more sensitive to oxidation to sulfate than SO_2.

Table XXXIII

Sorption-Regeneration of SO_2-N_2-Water Vapor on SSQ

Experiment C

Cycle No.	Gain g/g	Remaining after Regeneration, g/g
1	0.2277	0.0092
2	0.2416	0.0128
3	0.2213	0.0167
4	0.2338	0.0192
5	0.2401*	0.0472
6	0.2352	0.0495
7	0.2212	(0.0491 @ 95°C) (0.0480 @ 115°C)
8	0.2200	0.0500

Conditions:

Sorption: 7,700 ppm SO_2, 80,000 ppm H_2O, N_2, 55°C, 271 ml./min.

Regeneration: Dry N_2, 271 ml./min., 95°C

*Sample allowed to stand at room temperature 18 hours before regeneration.

SO_2-CO_2-O_2-NO-H_2O-N_2

As might be expected from the preceding results, the greatest NTD accumulation occurs when both NO and H_2O are present in the gas stream. In this situation, not only is there the necessary oxygen in the gas stream, but there is also the catalyst (NO), and the SO_2 is in the more easily oxidized form (HSO_3^-). Although data on pure SSQ with this gas mixture is not available, Section 4.2.2 shows the heavy accumulation of NTD from 3 cycles on a 42.4% polypropylene-SSQ fiber.

4.2.2 NTD Formation - Temperature Effect

At 55°C sorption temperature the total NTD accumulation for three cycles (30.2 hr. contact time with simulated flue gas) was 0.022 g/g fiber. At 95°C sorption temperature the total NTD accumulation for nine cycles (47.75 hr. contact time) was only 0.0013 g/g fiber. Tables XXXIII and XXXIV, Figure 7)

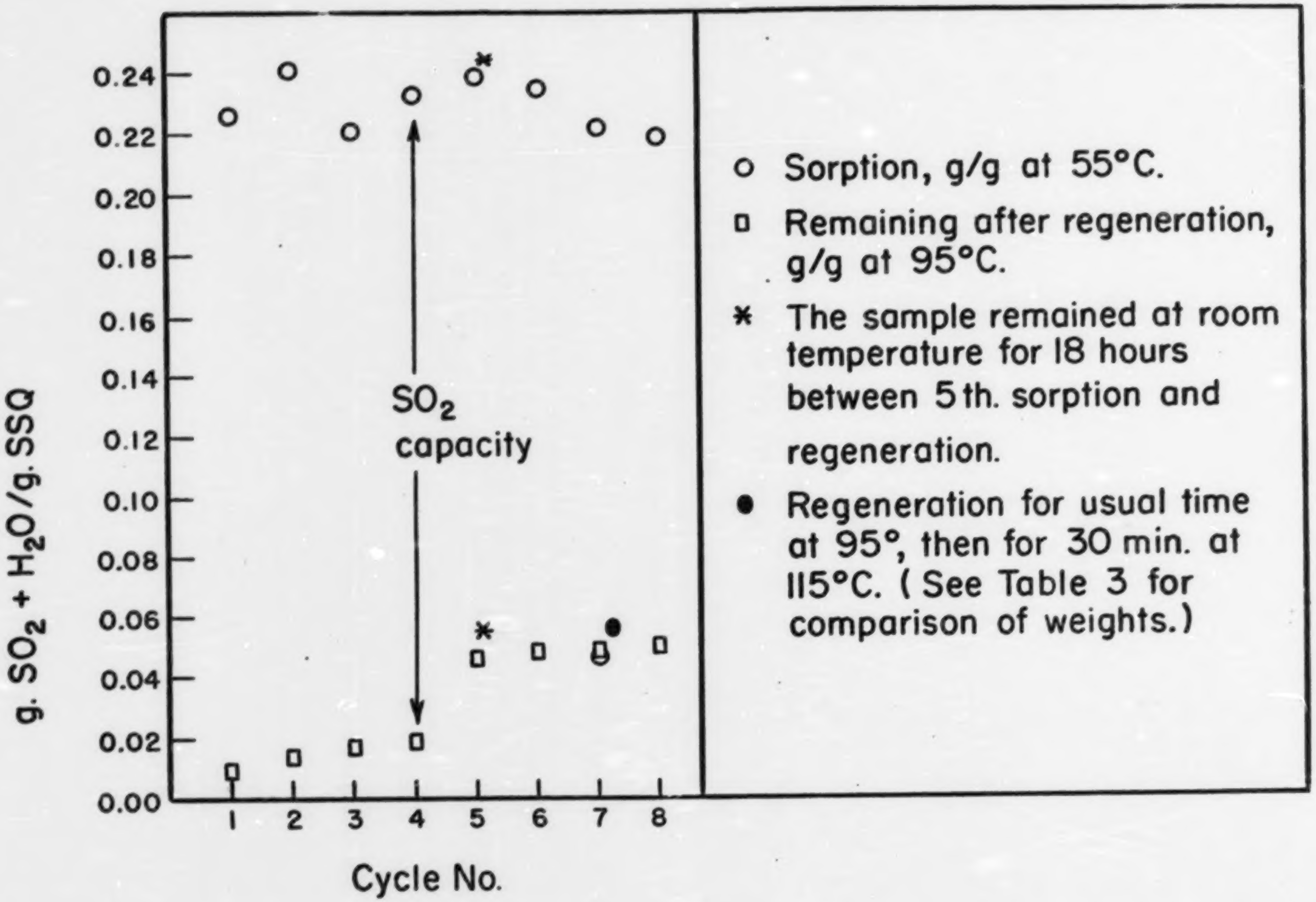


Fig. 16 - SO_2-N_2-water vapor on SSQ

Table XXXIV

Sorption-Regeneration of Wet, Simulated Flue Gas on SSQ-Polypropylene Fiber 124B

(drawn 5:1) (42.2% SSQ)

Cycle No.	Total Sorption Time, hrs.	Gain During Sorption g/g Fiber	Remaining after Regeneration g/g Fiber
1	0.38	.0069	
	0.66	.0096	
	1.83	.0205	
	3.00	.0303	
	4.00	.0377	
	5.17	.0444	.0112
2	1.17	.0170	
	1.83	.0207	
	3.00	.0278	
	4.00	.0306	
	4.75	.0348	.0038
3	4.72	.0135	
	12.60	.0292	
	20.28	.0387	.0066

Conditions:

Sorbent: 5.3783 g drawn (5:1) SSQ-Polypropylene Fiber 124B (42.2% SSQ)

Sorption: Feed gas: Simulated Flue Gas

Flow rate: Cycles 1, 2, 4 271 ml./min. (space velocity 3518 hr^{-1})
Cycle 3 21.2 ml./min. (space velocity 275 hr^{-1})

Temperature: 55°C

Regeneration:

Feed gas: dry N_2
Flow rate: 271 ml./min.
Temperature: 95°
Time: 3 hrs.

On the basis of the total SO_2 "handled" (sorbed and desorbed) by the fiber over the entire series of cycles, the NTD accumulation at 95°C was a much smaller fraction of the total SO_2 handled than in the 55°C experiment. These results are summarized in Table XXXV.

Table XXXV

NTD Accumulation at 55°C and 95°C

Fiber	%SSQ	Sorption Temp.	Total SO_2 (g/g fiber)	Total NTD (g/g fiber)	NTD as % of Total SO_2	Total Contact Time (Hr.)	Average g NTD/ g fiber/ Hr.	Total Cycles
129D	60.0	95°C	0.0941	0.0013	1.38	47.75	2.72×10^{-5}	9
124B	42.2	55°C	0.1179	0.0216	18.4	30.20	71.6×10^{-5}	3

In practice, the NTD accumulation at 95°C could be reduced even further by reducing the contact time; saturation at 95°C is reached rapidly (<1 hr.) and further contact with the flue gas after this time does not produce any appreciable additional sorption, but probably does produce additional NTD.

4.2.3 Identification of NTD Material

The economic importance of the total regenerability of SSQ (including the removal of NTD material) is self-evident. Hence we undertook the identification and characterization of the NTD material and a study of its removal from SSQ as well as polypropylene-SSQ fibers. An outline of this work follows.

(a) Simulation of multiple cycle process by means of a single long-term cycle.
   (1) Comparison with multiple cycle process.
(b) Spectrochemical analyses:
   (1) Infrared: $-NH^+$ absorptions
   (2) Ultraviolet: comparison of absorption maxima and extinction coefficients
(c) Titration curves
   (1) Shape of curve
   (2) Neutralization equivalent values
(d) Preparation of known sulfate-SSQ
   (1) Comparison of IR, UV, titration curves and chemical analyses
(e) Regeneration of NTD materials via alkaline hydrolysis
   (1) Determination of SO_4 as $BaSO_4$
   (2) Positive identification of $BaSO_4$ via X-ray powder pattern

4.2.3.1 Preparation of Non-Thermally Desorbable (NTD) Materials

The accumulation of a sulfur-containing material on SSQ after repeated sorption-regeneration processes with flue gas leads to loss of SO_2-sorption capacity. Before more detailed studies of this NTD material could be carried out, sufficient test materials had to be accumulated. Therefore, it was necessary that we simulate the multiple sorption (@ 55°C) - regeneration (@ 95°C) cyclic processes under less tedious circumstances. We accomplished this objective with the following materials: (a) SSQ and (b) a 14.25% polypropylene-SSQ fiber (112C).

(a) "NTD-SSQ" (CWL-Ap-106-A) was prepared by exposing SSQ (60-100 mesh) to a simulated flue gas mixture (SO_2, O_2, CO_2, NO, N_2, H_2O) at room temperature for 15.75 hrs., followed by a 5 hr. regeneration process at 100°C under a nitrogren atmosphere. Table XXXVI shows an accumulated g/g SSQ increase of 0.1769 (9.22% increase on wt. of 2.64 g sample of SSQ).

Table XXXVI

Sorption-Regeneration of SSQ (CWL-Ap-106-A)

	Sample	Sorption:
	2.3965 g SSQ	SO_2, CO_2, O_2, NO, N_2, H_2O vapor
	Sorption Time at Rm. Temp.	g/g SSQ
Cycle 1	9.75 hrs.	0.4898
	Regeneration Time at 87°-107°C	
	1 hr.	0.1715
	Sorption Time at Rm. Temp.	
Cycle 2	1.75 hrs.	0.3438
	3.00 hrs.	0.4199
	4.00 hrs.	0.4539
	5.75 hrs.	0.4961
	8.75 hrs.	0.5182
	11.75 hrs.	0.5412
	13.75 hrs.	0.5599
	15.75 hrs.	0.5654
	Regeneration at 98°-101°C	
	5 hrs.	0.1769

The SSQ after this treatment was in the form of orange-yellow aggregates. The amount of water removable by drying at 100°C/0.5 mm Hg overnight over P_2O_5 was 1%.

The infrared spectrum of the orange-yellow aggregates is superimposable upon the spectrum of RF-Ap-68, an "old non-regenerated" sample [dry SSQ, premix SO_2-5000 ppm (6/5/68)]. (See Figure 17) Comparison with the infrared spectra of RF-Ap-104 (SSQ-dry flue

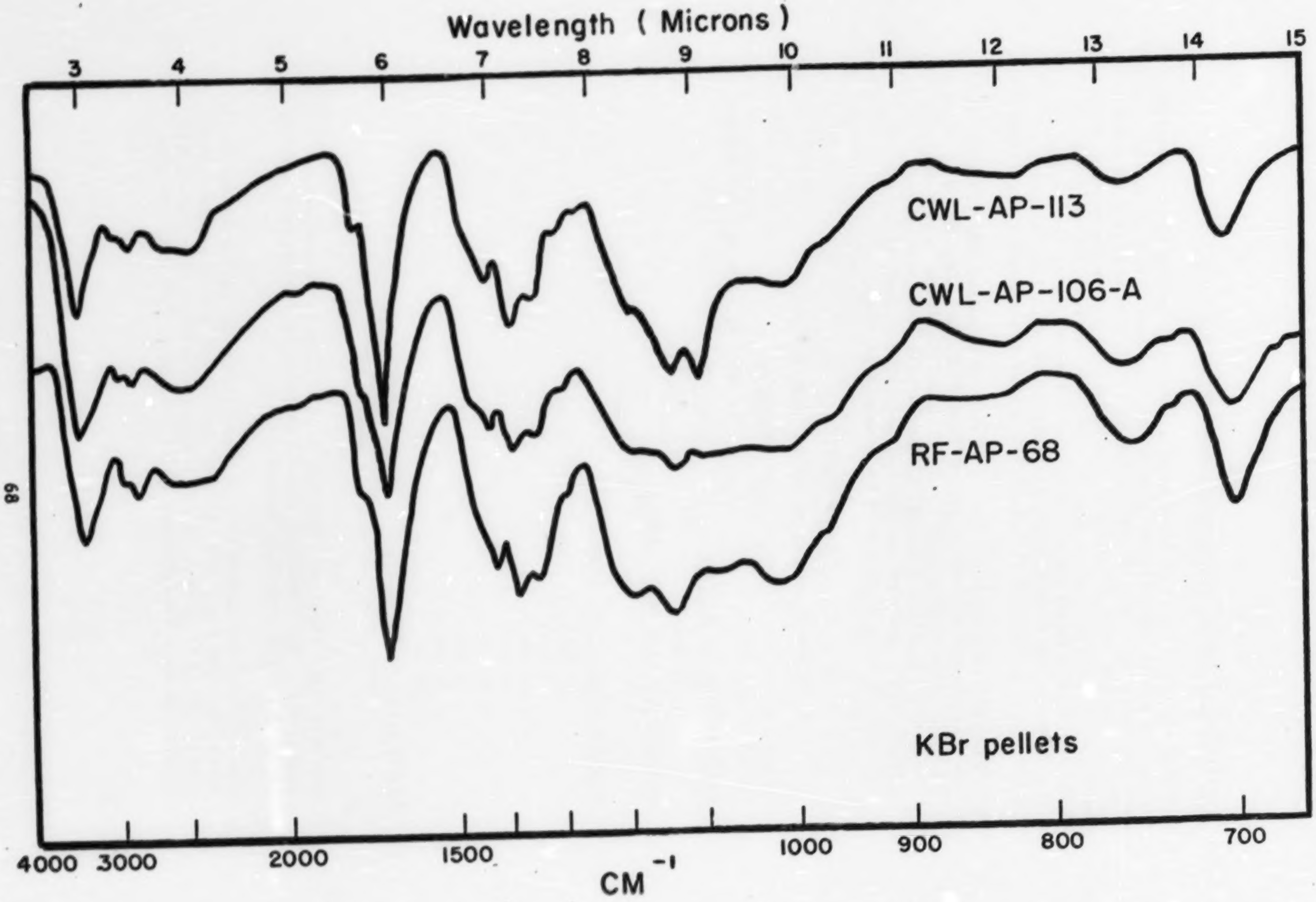


Fig. 17 - Comparison of H_2SO_4-SSQ (CWL-Ap-113) with NTD-materials - CWL-Ap-106-A (single long cycle) and RF-Ap-69 (old non-regenerated sample)

gas - 9 cycles) and RF-Ap-105 (SSQ-wet SO_2-N_2 - 8 cycles) shows differences in the 3000-2300 cm^{-1} region. (see Figure 18) The broad absorptions in this region found in orange-yellow aggregates (CWL-Ap-106-A) are indicative of acids or $-NH^+$ type absorptions. This supported our postulate that $-NH^+HSO_4^-$ structures exist in the NTD-containing materials.

It is probable that at lower reaction temperatures (room temperature vs. 55°C) the conditions for forming NTD materials are more favorable, i.e., stability of the SO_2:N- complex, the bisulfite salt, and the water content is such that the formation of $-NH^+HSO_4^-$ is favored at room temperature. At higher temperatures (55°C) the amount of water vapor sorbed, and the residence time of SO_2 and other species on the tertiary amine nitrogen is short and the side reactions involving NO, NO_2, O_2 or H_2O are not favored.

(b) "NTD/polypropylene-SSQ fiber" (CWL-Ap-108-A) was similarly prepared by exposing a 3.74 g sample of 14.25% polypropylene-SSQ fiber (RF-Ap-112C) to a gaseous mixture of SO_2, CO_2, N_2, and H_2O vapor for 15 3/4 hrs. at room temperature. NO was left out of the mixture. The sample was carried through a complete cycle by regenerating at 96°C over 3 hrs. under N_2 atmosphere. Table XXXVII illustrates an accumulated g/g fiber increase of 0.0249 and g/g SSQ increase of 0.1749 as compared with a g/g SSQ of 0.1769 for CWL-Ap-106A. (See Figures 19, 20)

Table XXXVII

Sorption-Regeneration of 14.25%
SSQ-Polypropylene Fiber (CWL-Ap-108-A)

Sample: 3.74 g of RF-Ap-112-C (14.25% SSQ-polypropylene fiber)

Sorption: SO_2, O_2, CO_2, N_2, H_2O vapor

Sorption Time	g/g fiber	g/g SSQ
2 hrs.	0.0565	0.3965
10 hrs.	0.0979	0.6868
15.75 hrs.	0.1093	0.7669
Regeneration Time		
1 hr.	0.0278	0.1954
3 hrs.	0.0249	0.1749

Since the accumulation of NTD materials in the presence of water vapor occurs in both the presence and the absence of oxides of nitrogen, we compared the NTD materials produced in example (a) with those produced in (b) and found that these NTD materials were essentially the same. This shows that NTD accumulation does not necessarily require the presence of NO. The "old non-regenerated" sample (RF-Ap-68) is another example of the formation of NTD in the absence of NO. It appears that NTD formation can occur via at least the folowing two pathways.

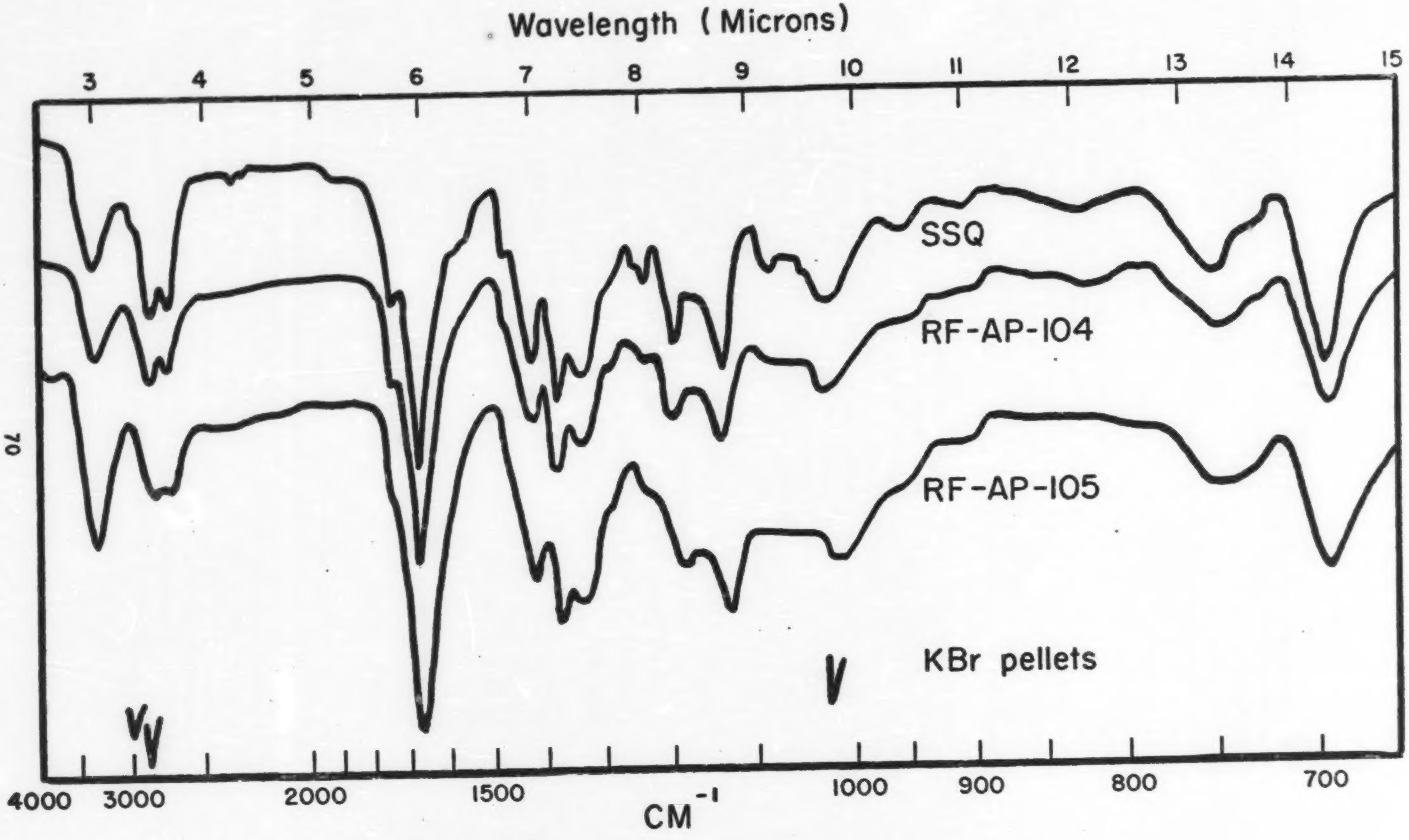


Fig. 18 - Comparison of SSQ with RF-Ap-104 and RF-Ap-105

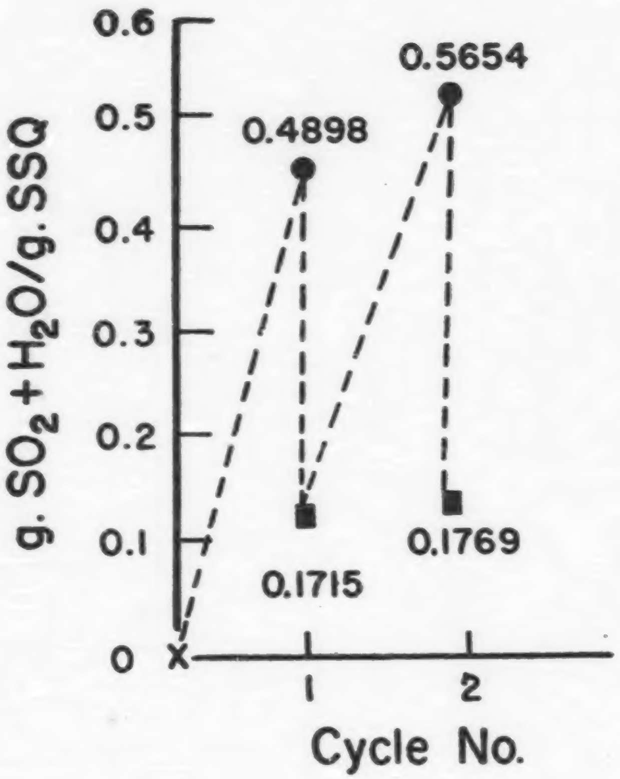


Fig. 19 - Sorption-regeneration on SSQ (CWL-Ap-106-A)

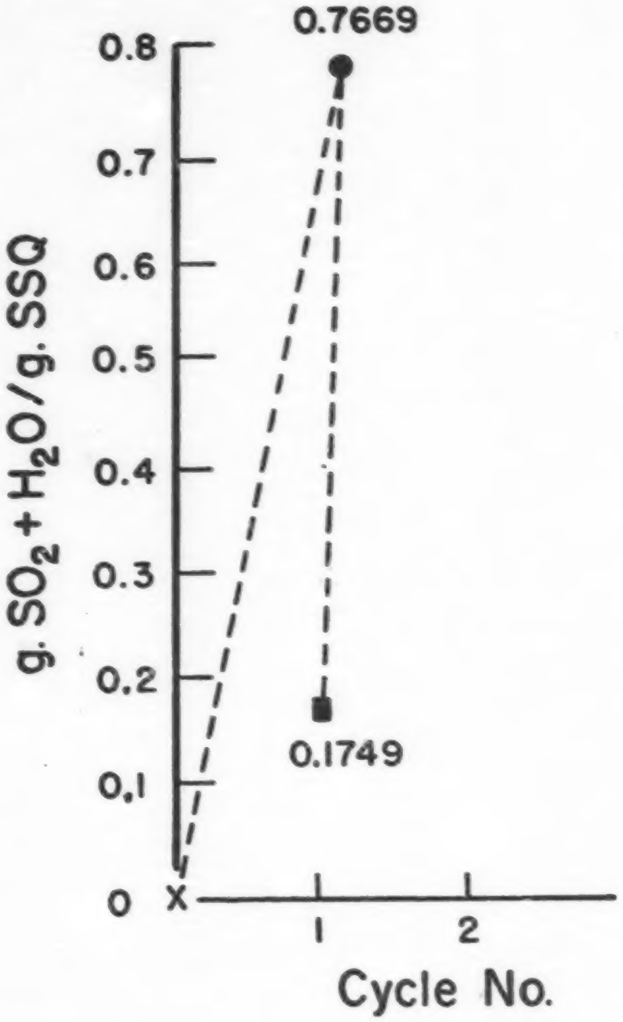
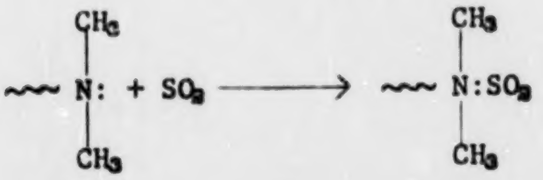


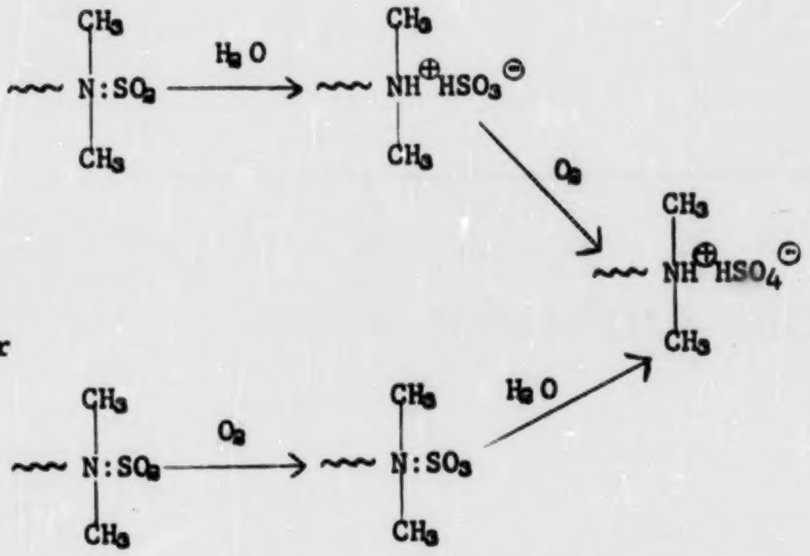
Fig. 20 - Sorption-regeneration on 14.25% SSQ-polypropylene fiber (CWL-Ap-108-A)

In the case of the non-regenerated sample (RF-Ap-68 - dry SSQ, premix SO_2 5000 ppm) that was allowed to stand for 6 months, the following is possible:



$$\sim\!\sim\!\sim N(CH_3)_2: + SO_2 \longrightarrow \sim\!\sim\!\sim N(CH_3)_2:SO_2$$

Lewis Acid-Base Complex



$$\sim\!\sim\!\sim N(CH_3)_2:SO_2 \xrightarrow{H_2O} \sim\!\sim\!\sim NH^{\oplus}(CH_3)_2\,HSO_3^{\ominus} \xrightarrow{O_2} \sim\!\sim\!\sim NH^{\oplus}(CH_3)_2\,HSO_4^{\ominus}$$

or

$$\sim\!\sim\!\sim N(CH_3)_2:SO_2 \xrightarrow{O_2} \sim\!\sim\!\sim N(CH_3)_2:SO_3 \xrightarrow{H_2O} \sim\!\sim\!\sim NH^{\oplus}(CH_3)_2\,HSO_4^{\ominus}$$

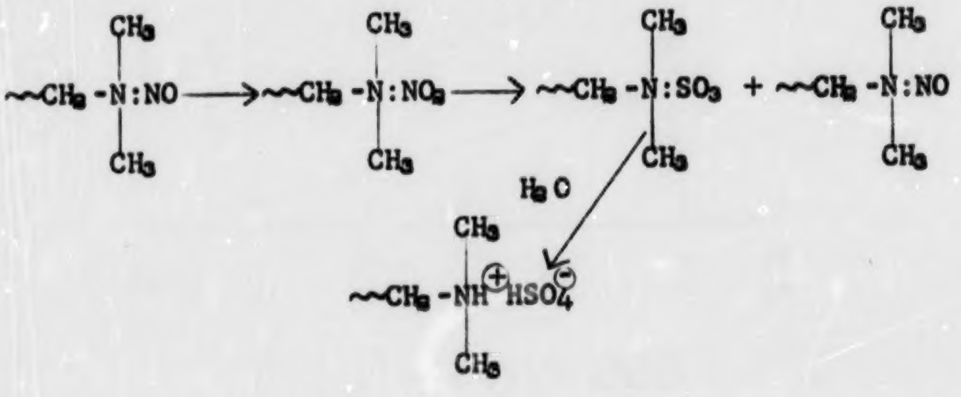
If NO is present, the following may occur as well:

$$NO + O_2 \longrightarrow NO_2$$

$$NO_2 + SO_2 \longrightarrow SO_3 + NO$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

As mentioned in Section 4.2.1, the sorbent may facilitate the process in the following manner:



$$\sim CH_2\text{-}N(CH_3)_2:NO \longrightarrow \sim CH_2\text{-}N(CH_3)_2:NO_2 \longrightarrow \sim CH_2\text{-}N(CH_3)_2:SO_3 + \sim CH_2\text{-}N(CH_3)_2:NO$$

$$\sim CH_2\text{-}N(CH_3)_2:SO_3 \xrightarrow{H_2O} \sim CH_2\text{-}NH^{\oplus}(CH_3)_2\,HSO_4^{\ominus}$$

4.2.3.2 Spectrochemical Analyses

Infrared Spectroscopy - The initial NTD-SSQ samples (RF-Ap-104 and RF-Ap-105) showed no spectrochemical differences from SSQ itself (see Figure 18). However, melting point determinations showed them to be quite different from SSQ. For example:

Sample	m.p. Range °C
SSQ	142-182
RF-Ap-104	192° darkens, does not soften or melt <305°C
RF-Ap-105	190° darkens, does not soften or melt <305°C

It was not until an old non-regenerated sample (RF-Ap-68) was examined did we observe spectrochemical differences. These differences were indicative of acid or $-NH^+$ type absorptions (2300-3000 cm^{-1} in IR). We later showed RF-Ap-68 to be an SSQ-H_2SO_4 salt while RF-Ap-104 and RF-Ap-105 are samples containing smaller quantities of SSQ-H_2SO_4 which evidently are not detectable in the IR. Their solubility properties support this conculsion (See Scheme I). Another possibility we considered is that they may also contain $-N:SO_3$.

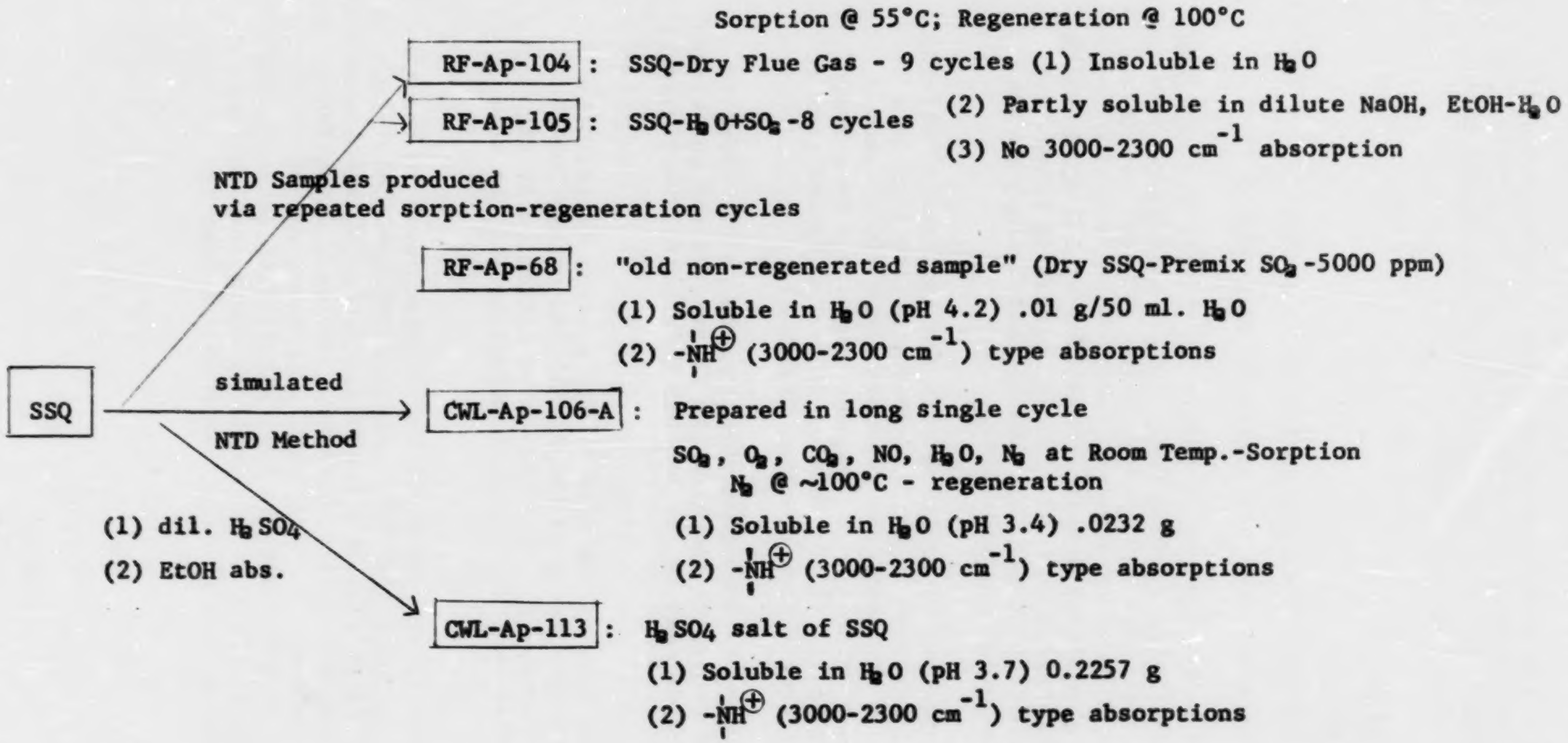
Comparison of the IR spectrum of RF-Ap-68 with the spectrum of NTD-SSQ materials (CWL-Ap-106) prepared by using a long reaction time in a single cycle (sorption @ rm. temp. and regeneration @ 100°C) showed them both to be the same material. Subsequent comparison to a known reference compound CWL-Ap-113 (H_2SO_4 salt of SSQ) also showed them to be identical to the reference compound (See Figure 17).

Ultraviolet Spectroscopy - To show that substitution on the aromatic nucleus of SSQ did not occur, we compared the UV spectra and calculated extinction coefficients of each of the SSQ-NTD materials (See Figure 21 and Scheme II).

The striking similarity between the ultraviolet spectra (especially the molar extinction coefficients) of CWL-Ap-113 and CWL-Ap-106-A indicates two things, namely, (1) sulfonation or nitration of the aromatic nucleus is ruled out, and (2) both materials are the same thing.

The $-NH^{\oplus}$ type absorption in the 3000-2300 cm^{-1} region found in the IR spectra of RF-Ap-68 (old non-regenerated sample), CWL-Ap-106-A (simulated single-cycle NTD material) and CWL-Ap-113 (H_2SO_4-SSQ salt) show that these materials are very likely the same. The only differences are in the amount of $-NH^{\oplus}HSO_4^-$ in each sample. Absence of $-NH^{\oplus}$ absorptions in samples RF-Ap-104 and RF-Ap-105 indicates insignificant amounts of bisulfate salt. This is reflected by their insolubility in water and partial solubility in dilute NaOH (See Scheme I).

Scheme I. Spectrum of SSQ Samples Containing Various Levels of Bisulfate NTD



Sorption @ 55°C; Regeneration @ 100°C

RF-Ap-104 : SSQ-Dry Flue Gas - 9 cycles (1) Insoluble in H_2O

RF-Ap-105 : SSQ-H_2O+SO_2-8 cycles

(2) Partly soluble in dilute NaOH, EtOH-H_2O

(3) No 3000-2300 cm^{-1} absorption

NTD Samples produced
via repeated sorption-regeneration cycles

RF-Ap-68 : "old non-regenerated sample" (Dry SSQ-Premix SO_2-5000 ppm)

(1) Soluble in H_2O (pH 4.2) .01 g/50 ml. H_2O

(2) $-\overset{|}{\underset{|}{N}}H^{\oplus}$ (3000-2300 cm^{-1}) type absorptions

SSQ

simulated

NTD Method

CWL-Ap-106-A : Prepared in long single cycle

SO_2, O_2, CO_2, NO, H_2O, N_2 at Room Temp.-Sorption
N_2 @ ~100°C - regeneration

(1) Soluble in H_2O (pH 3.4) .0232 g

(2) $-\overset{|}{\underset{|}{N}}H^{\oplus}$ (3000-2300 cm^{-1}) type absorptions

(1) dil. H_2SO_4

(2) EtOH abs.

CWL-Ap-113 : H_2SO_4 salt of SSQ

(1) Soluble in H_2O (pH 3.7) 0.2257 g

(2) $-\overset{|}{\underset{|}{N}}H^{\oplus}$ (3000-2300 cm^{-1}) type absorptions

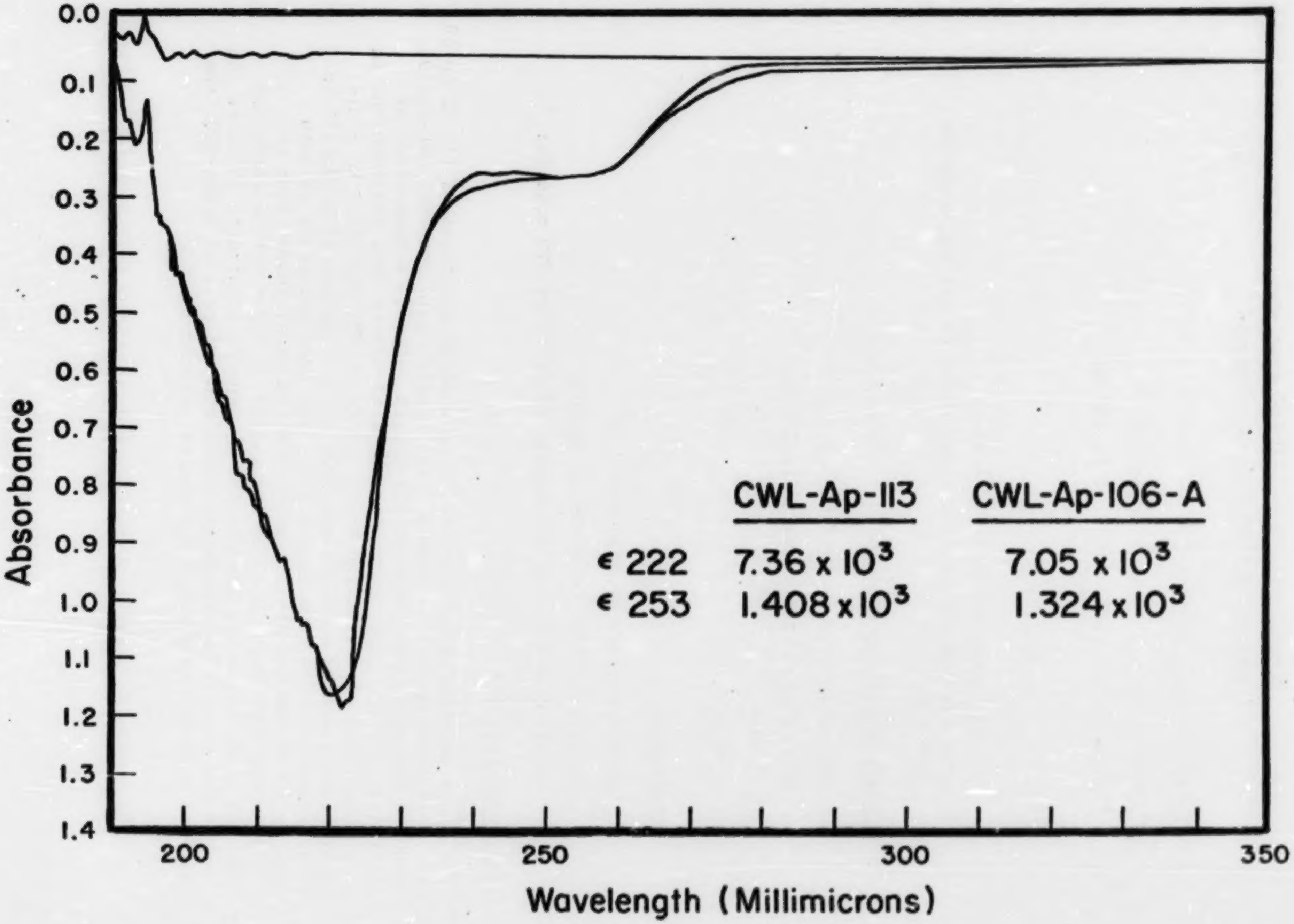


Fig. 21 - UV Spectra of CWL-Ap-113 and CWL-Ap-106-A

Scheme II

Identification of NTD-SSQ Material

Comparison with a Known Compound

I NTD-SSQ "One Cycle Method" CWL-Ap-106A

a. Neutralization equivalent 323.6

b. Ultraviolet data : λmax 222, 253 mμ

ϵ_{222} 7.045×10^3

ϵ_{253} 1.324×10^3

c. 66% SO_2-sorption capacity loss

d. Alkaline regeneration material recovers 91% SO_2-sorption capacity

II H_2SO4-SSQ Reference Compound : CWL-Ap-113

a. Neutralization equivalent 313.3

b. Ultraviolet data : λmax 222, 253 mμ

ϵ_{222} 7.36×10^3

ϵ_{253} 1.408×10^3

Conclusions

A. Both materials are the same

B. No substitution on aromatic nucleus

C. Alkaline hydrolysis is capable of removing NTD material

4.2.3.3 Titration Curves

The water solubility and the resulting acid pH solutions of (1) RF-Ap-68 the "old non-regenerated sample," (2) single-cycle material CWL-Ap-106 and (3) the reference compound CWL-Ap-113, allowed a comparison of titration curves. The neutralization equivalents were instrumental in our comparison of extinction coefficients of (2) and (3). We could conveniently assign a mechanism (base neutralization of a diacid) to the titration curve (See Figure 22). The base titration of both CWL-Ap-106-A and CWL-Ap-113 (reference compound) showed that an alkaline pH ($>$pH 9-10) must be maintained in order not to leach out the SSQ when fibers are regenerated by aqueous treatment, i.e., at the end of the base titration (phenolphthalein end pt.) of H_2SO4-SSQ, the SSQ was observed to precipitate out of solution.

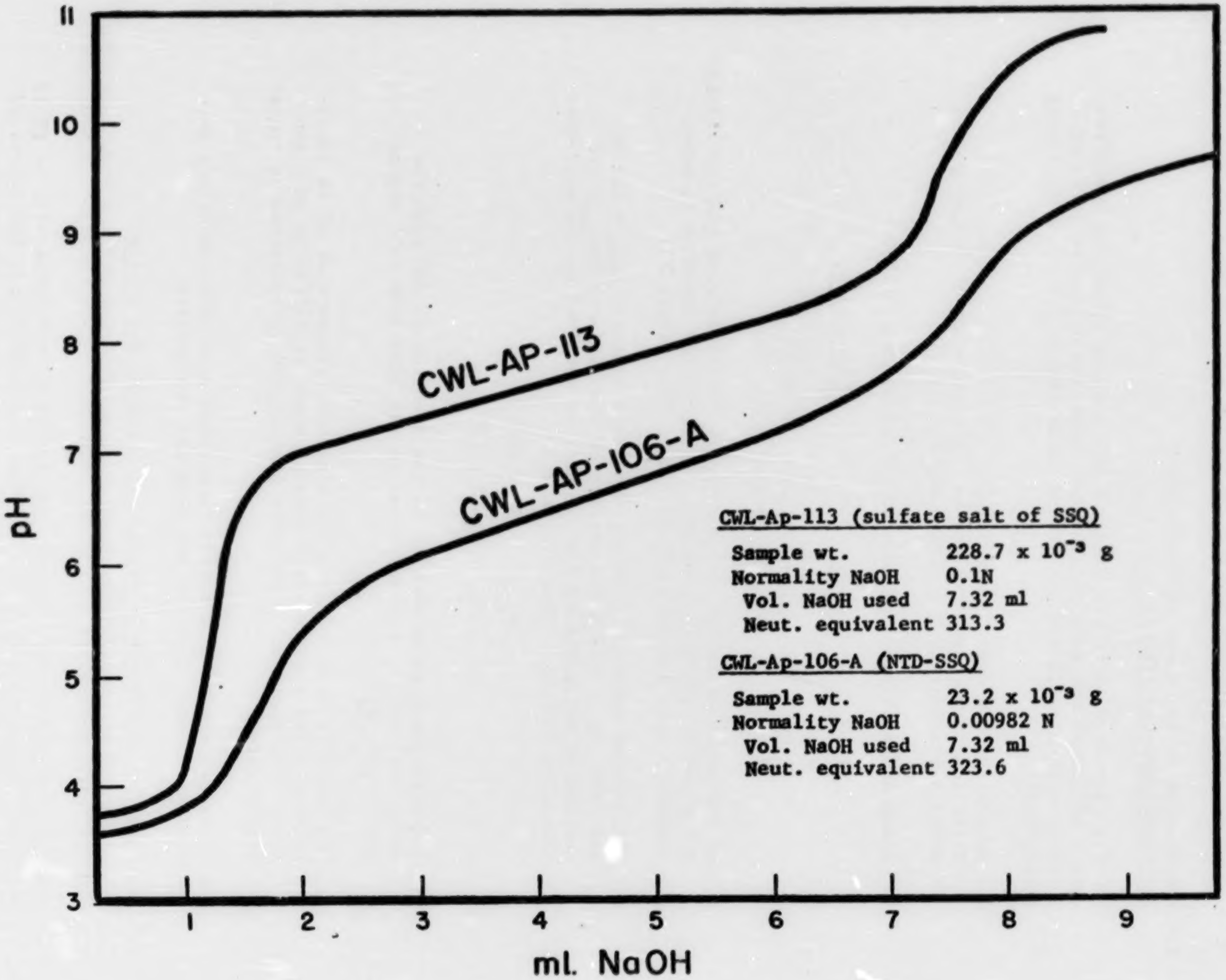


Fig. 22 - Titration curves of H_2SO_4-SSQ (CWL-Ap-113) and NTD-SSQ (CWL-Ap-106-A)

4.2.3.4 Preparation of the Known Sulfate -SSQ Reference Compound (CWL-Ap-113)

SSQ was dissolved in excess dilute H_2SO_4 and the resulting bisulfate salt ($-NH^{+}HSO_4-$) was precipitated from solution by the addition of absolute ethanol. This H_2SO_4-SSQ salt, CWL-Ap-113, has the following properties:

a. Neutralization equivalent: 313.3
Titration curve shows two breaks. The solution of 0.2287 g shows a starting pH 3.7. (See Figure 22)

b. Elemental analysis: Calculated on formula wt. of 386

	Found	Theoretical
% N	7.32, 7.34	7.31
% C	57.02, 56.91	53.26
% H	6.75, 6.83	6.00

c. At the phenolphthalein end pt. ~pH 10, a precipitate (CWL-Ap-113-B) forms and is identified as SSQ. Its infrared spectrum is superimposable upon spectrum of SSQ itself (See Figure 23).

d. Ultraviolet spectrum in water shows two maxima. $\lambda_{max} = 222$ mμ and 253 mμ. The molar extinction coefficients ($\epsilon\lambda_{max}$) are calculated using the equivalent wts. as obtained by the acid-base titration (313.3). (See Figure 21)

$$\epsilon_{222} = 7.36 \times 10^3$$
$$\epsilon_{253} = 1.408 \times 10^3$$

e. Infrared spectrum is similar to the spectrum of SSQ with the additional $-NH^+$ type absorptions in the 3000-2300 cm^{-1} region. (See Figure 23)

f. The filtrate obtained from the alkaline treatment at pH 10 (maintained) gives a white solid ($BaSO_4$) **when** acidified to pH 2 and mixed with $BaCl_2$ solution under heating.SSQ is recovered in regenerated form.

The above properties in a direct comparison with other materials gave conclusive evidence that the NTD material was sulfate.

4.2.4 Regeneration of NTD-SSQ Materials via Alkaline Hydrolysis

Elemental Analyses

Alkaline hydrolysis of RF-Ap-68, CWL-Ap-106-A, and CWL-Ap-113 at pH 10 all gave "recovered SSQ." In the case of CWL-Ap-106-A, the recovered SSQ was tested and found to have 91% of its original SO_2 sorption

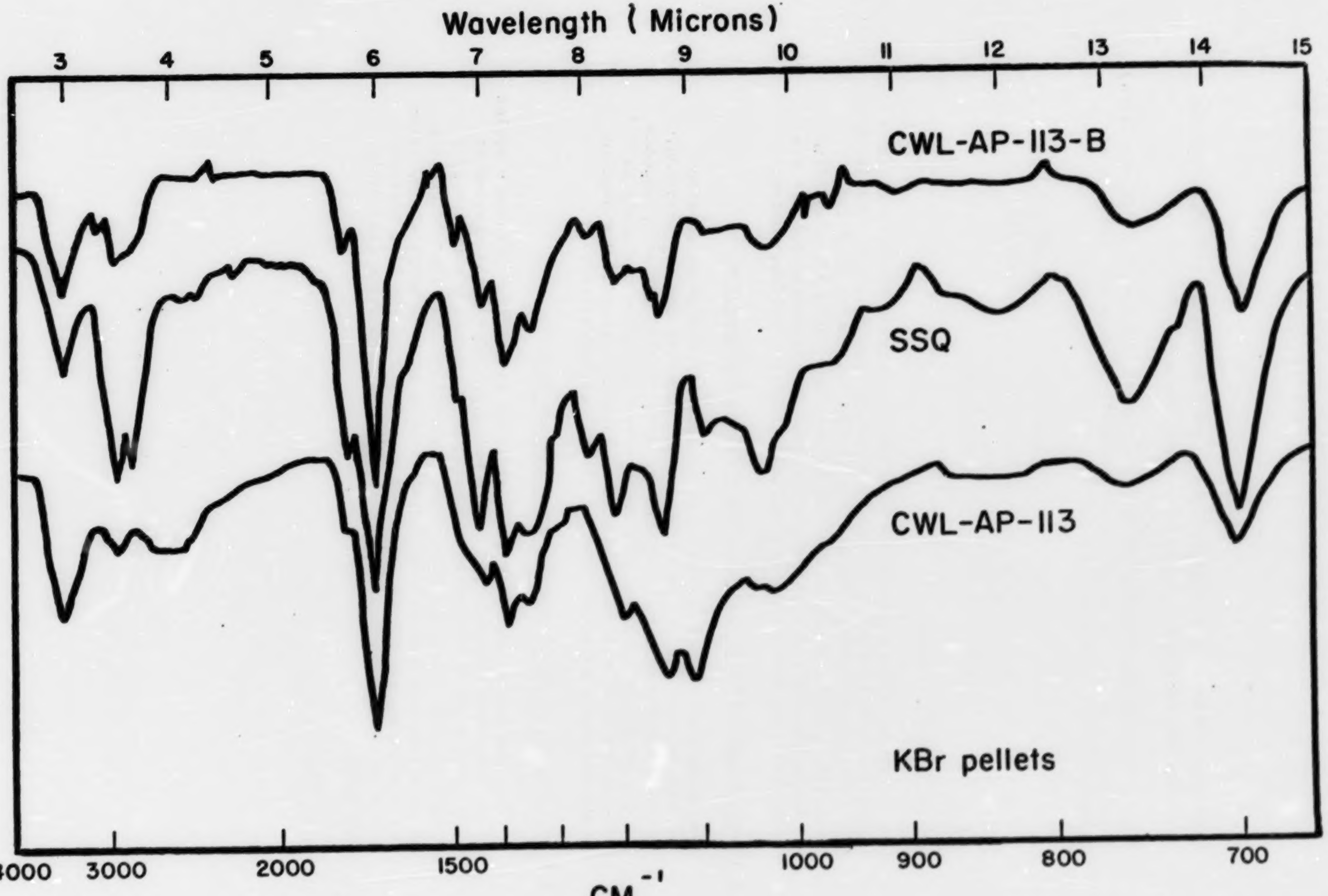


Fig. 23 - Comparison of SSQ, SSQ-H_2SO_4 salt (CWL-Ap-113), and SSQ recovered from alkaline hydrolysis of CWL-Ap-113 (CWL-Ap-113-B)

capacity. This sample (CWL-Ap-106-A) had lost 66% of its SO_2 sorption capacity due to NTD accumulation. (See Scheme I)

The "recovered SSQ" from alkaline regenerated CWL-Ap-106-A (CWL-Ap-111-A) was compared with SSQ itself via elemental analyses and found to be quite similar. (Also see Figure 17)

	SSQ (RF-388)	CWL-Ap-111-A	SSQ (MF-4-69)
% N	9.93, 9.84	9.34, 9.24	9.39,940
% C	71.45, 71.30	72.42, 72.2	
% H	7.87, 7.79	7.70, 7.80	

Sulfate Determination

The filtrates obtained from the alkaline hydrolysis (@ pH10) of the H_2SO_4-SSQ salt (CWL-Ap-113) and a polypropylene-SSQ fiber containing NTD yield white solids ($BaSO_4$) after acidification to pH 2 and addition of $BaCl_2$ solution (5%) under heating. Both are identified as $BaSO_4$ via their X-ray powder pattern. The recovered sulfate was essentially quantitative based on the calculated sulfate content.

4.2.5 Restoration of Fiber Capacity via Alkaline Regeneration

The identification of the NTD material now allowed us to develop methods for the restoration of the fiber capacity for SO_2-sorption. Initially the preliminary experiments were carried out using aqueous sodium hydroxide solution. We later screened sodium carbonate as well as ammonium hydroxide solutions. Sodium carbonate was used to study the efficiency and rates of removal of NTD-sulfate.

4.2.5.1 Restoration of Fiber Capacity with Aqueous NaOH

A fiber containing 14.25% SSQ (fiber 112C) was carried through 9 cycles of sorption and regeneration with a wet 0.77% SO_2-N_2 gas mixture at 55°C. The loss in thermally regenerable SO_2 capacity over the nine cycles was 30%. A relatively mild treatment of the fiber consisting of stirring with 0.02 N NaOH for 45 minutes at room temperature, washing with water and drying, restored almost 2/3 of the lost capacity. The experimental conditions were the same in each cycle (See Table XXXVIII).

Table XXXVIII

Chemical Regeneration of Polypropylene-SSQ Fiber

Cycle No.	Regenerable $SO_2 + H_2O$ Capacity (g/g)	Contact Time With Feed Gas (Minutes)
1	0.033	266
2	0.030	248
9	0.023	259
Aqueous NaOH Treatment		
10	0.029	266
11	0.027	266

Feed gas 0.77% SO_2, 8% H_2O vapor, N_2; 55°C; 271 ml./min.

Efforts were then directed to application of this treatment to fibers containing NTD produced by simulated flue gas, and to optimization of the treatment procedures.

The assessment of methods for chemical regeneration of polypropylene-SSQ fibers to remove NTD material and thereby restore SO_2-sorption capacity requires a knowledge of the efficiency with which NTD-sulfate can be removed via alkaline regeneration. This knowledge was obtained by determining the rate at which sulfate is removed from the NTD fiber at 80°C with Na_2CO_3 solution.

4.2.5.2 Efficiency of NTD-Sulfate Removal via Alkaline Carbonate Treatment

The efficiency of removal of NTD-sulfate from polypropylene-SSQ fiber is important for practical use of the fiber for sorption-regeneration purposes. The effect of temperature on the efficiency of NTD removal was studied.

Effect of Temperature on Sodium Carbonate Regeneration of NTD Fiber

Two portions (A) and (B) of sample CWL-Ap-116-B were treated with 50 ml. of 0.1 N sodium carbonate at different temperatures to determine the efficiency to remove NTD materials.

Both samples (A) and (B) were presoaked in 50 ml. of 0.1N Na_2CO_3 solution after they had been chopped in a Waring Blendor. During the presoaking period the fibers were periodically stirred with a glass rod. Sample A was subsequently heated at 80°C for 1 hr., while Sample B was allowed to stand at room temperature under constant stirring. The difference in the efficiency of sulfate removal between the methods is 3.8%. (See Scheme III)

Scheme III

Effect of Temperature on the Efficiency of Sulfate Removal by Aq. Sodium Carbonate

Experiment CWL-Ap-116-B: 42% SSQ undrawn fiber, containing NTD g/g fiber = 0.0629

(a) Sample A (1.358g) fiber
(b) Sample B (1.3615 g) fiber

Both fibers presoaked at rm. temp. for 1 hr. in 0.1N Na_2CO_3 (50 ml.)

A: heated at 80°C for 1 hr.
B: stirred at rm. temp. for 1 hr.

Calculations

NTD Content of Each Sample of Fiber

(A) 1.358 g x 0.0629 g/g fiber - 0.085418 g NTD material

(B) 1.3615 g x 0.0629 g/g fiber = 0.085638 g NTD material

Corresponds to the following moles of H_2SO_4 (f.w. 98):

(A) 8.7161×10^{-4} mole H_2SO_4 (B) 8.7385×10^{-4} mole H_2SO_4

Corresponds to the following weight of $BaSO_4$ (f.w. 233):

(A) 0.20308 g expected (B) 0.2034 g expected

Actual $BaSO_4$ obtained:

(A) 0.160 g (B) 0.1525 g

Therefore the % Removal of $SO_4^{=}$ or the % Recovery of SSQ capacity:

(A) 78.78% (B) 74.9%

Difference of 3.81%

A similar sample C was presoaked at room temperature for 15 min. and then heated at 80°C for 1.5 hr. The % removal of $SO_4^{=}$ or % recovery of SSQ capacity was 80.93%.

Rate of NTD-Sulfate Removal with Sodium Carbonate Solution

In order to determine the rate at which NTD-sulfate is removed, we carried out the following experiment on a sample of polypropylene-SSQ fiber whose SO_2-sorption ability had been reduced to zero by means of the single-cycle long-exposure process referred to previously. We will refer to this sample as CWL-Ap-121. (It was undrawn fiber RF-Ap-124-B, 42.8% SSQ)

Method - Sample 121-A (1.554 g) and 121-B (1.5570 g) were presoaked in 50 ml. of 0.1N Na_2CO_3 for 15 minutes at room temperature then heated at 80°C for specific intervals and tested for sulfate removal by determination as $BaSO_4$, e.g., 121-A was heated for a total period of 195 mins. at 80°C. The alkaline filtrates were removed by suction filtration and tested for sulfate content at intervals of 15 mins., 45 mins., 75 mins. and 195 mins. 121-B was similarly tested (heating for a total time of 180 mins.) at intervals of 30 mins., 60 mins., and 180 mins. (See Figure 24)

Discussion - In both cases, the rate of NTD-sulfate removal was similar. However, the addition of a small amount of a nonionic surfactant (Triton X-100) to the alkaline solution apparently increased the rate of NTD-sulfate removal as $BaSO_4$. This is understandable since wetting of the fiber was increased. The increased rate is shown in Figure 24. The slope of the line after 60 and 75 minutes is much steeper than the previous part of the curve. However, the maximum level of sulfate removal was only 65% after 195 minutes. We later discovered that the alkaline hydrolysis with sodium hydroxide and sodium carbonate was incomplete. Ammonium hydroxide solutions (0.1N) removed all of the remaining sulfate. It appears that ammonium hydroxide possesses the ability to diffuse into the fiber to complete the removal of NTD-sulfate after the alkaline regeneration has been started with sodium hydroxide or sodium carbonate. Additional heating with sodium carbonate alone did not complete the removal as with ammonium hydroxide solution. Furthermore, removal of NTD-sulfate is not as effective with just ammonium hydroxide itself.

At this time, the removal of NTD-sulfate has not been entirely resolved. Each alkaline system alone or in combination with each other must be further studied in order to obtain a full understanding. However, the efficiency of NTD-sulfate removal is not as high as implied in this discussion, since in actual experience the SSQ-fibers would never attain the 100% incapacitation as in our test materials (e.g., CLW-Ap-121). The important point to be made here is that it is technically possible to remove all the NTD-sulfate and restore the SO_2-sorption capacity of the fibers.

4.2.5.3 Increased SO_2-Sorption Rates After Alkaline Regeneration

An interesting phenomenon was observed with alkaline-regenerated SSQ-fibers, namely, increased rates in SO_2-sorption. A possible explanation lies in an analogy to the increased dyeability of acid-activated polypropylene-polyvinylpyridine fibers, a proprietary Uniroyal process by which microscopic cracks or fissures are formed which allow the anionic dyes to diffuse throughout the fiber.

An electron photomicrograph study in the present case shows voids surrounding globular bodies that could allow facile diffusion of SO_2 to the SSQ. Such voids can be postulated to have occurred through (1) an expansion of the NTD-sulfate particles, (2) subsequent hydrolysis under basic conditions then (3) contraction with washing to regenerate the free-amine SSQ particles to their original size. The overall result would leave a void. (See Figures 25 and 26)

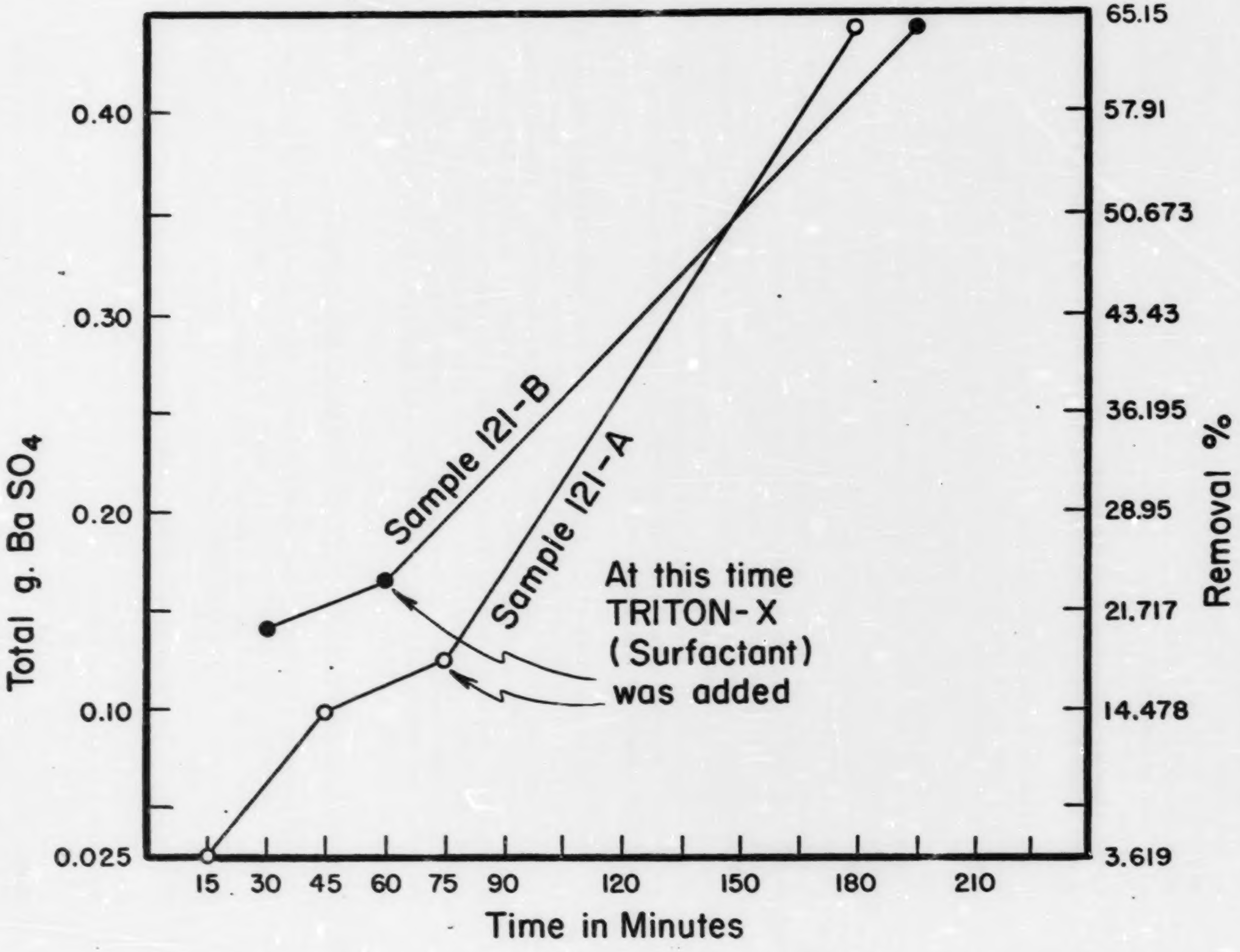


Fig. 24 - Rate of NTD-removal with aqueous sodium carbonate at 80°C.

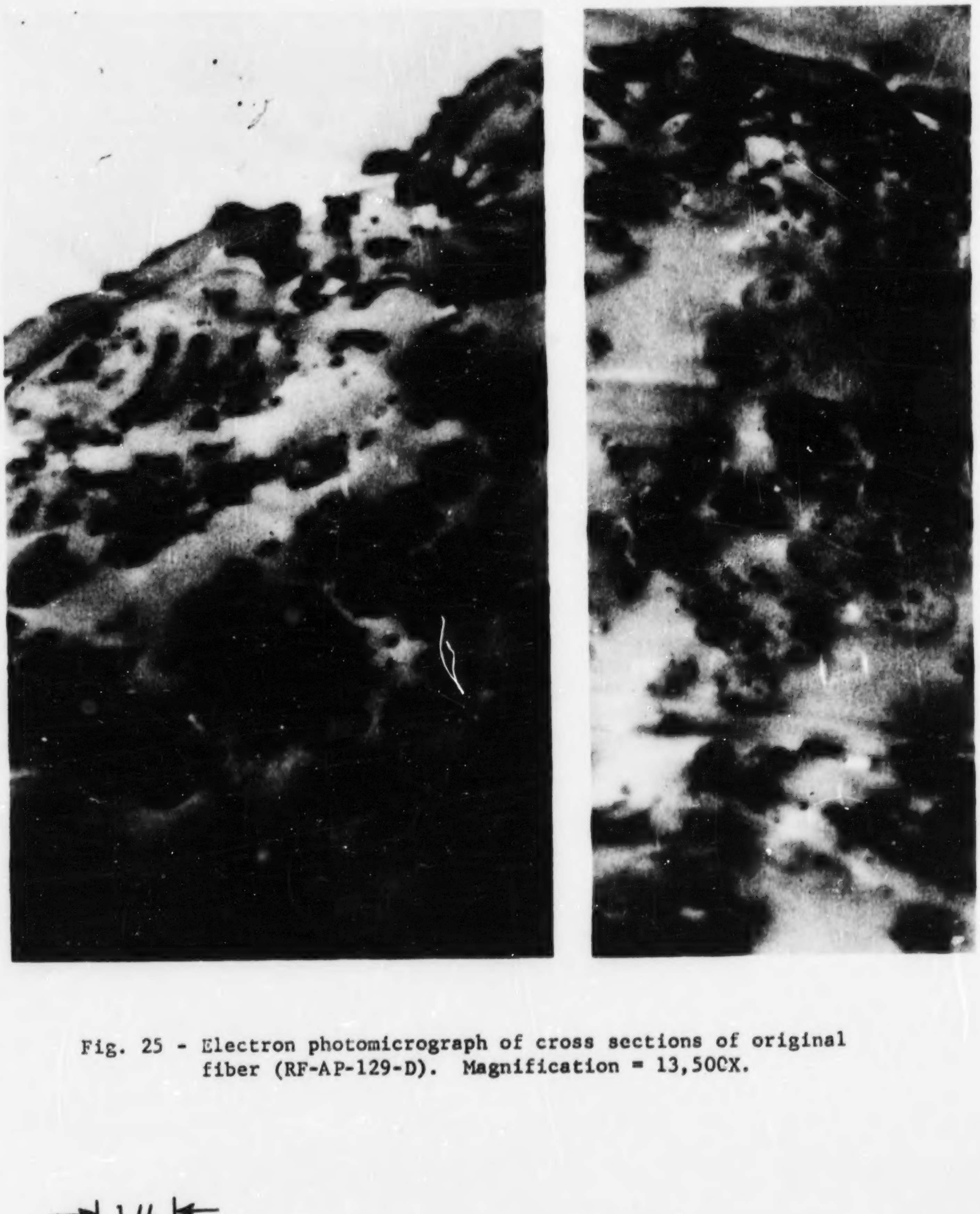


Fig. 25 - Electron photomicrograph of cross sections of original fiber (RF-AP-129-D). Magnification = 13,500X.

→| 1μ |←

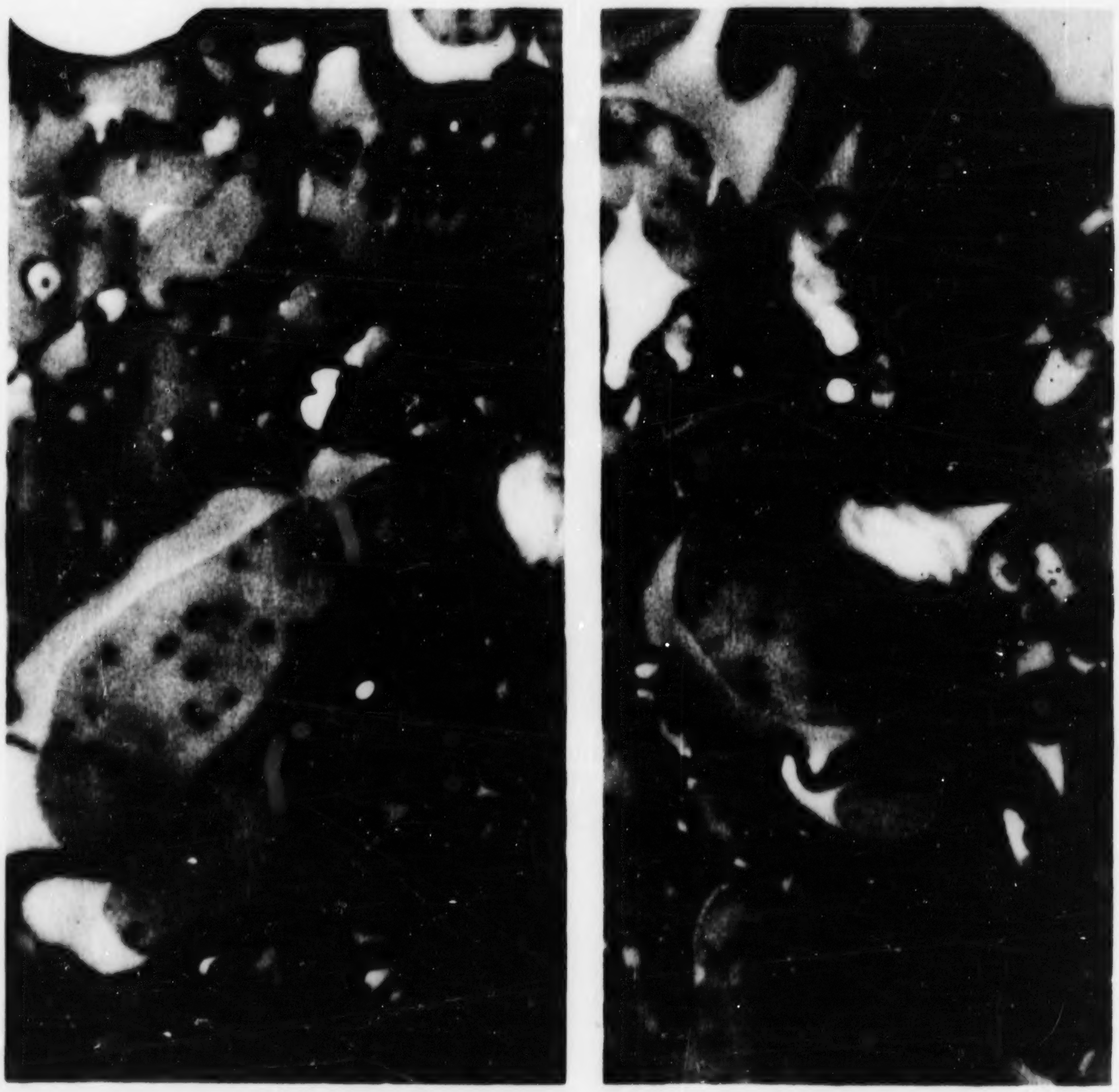


Fig. 26 - Electron photomicrograph of cross sections of alkaline regenerated fiber (NTD-RF-AP-129-D) showing formation of voids. Magnification = 13,500X.

—→| 1 μ |←—

5.0 ECONOMIC CONSIDERATIONS

We will consider the application of a sorbent process to a coal-fired steam plant of about 1100 megawatts capacity, emitting 2 x 10^6 SCFM of flue gas of the reference Composition I (Table XXXIX).

Table XXXIX

FLUE GAS COMPOSITION I

Component	Volume Percent	Pounds/Minute @ 2 x 10^6 SCFM	BTU/# °F	BTU/Min. °F @ 2 x 10^6 SCFM
N_2	74.9	108,800	0.25	27,200
CO_2	14.7	33,800	0.22	7,436
H_2O	7.25	6,800	0.45	3,060
O_2	2.8	4,640	0.22	1,021
SO_2	0.3	1,018	0.16	163
NO_x	0.05	78	0.23	18
	100.00	155,136		
Fly Ash (Wt.%)	0.2	310		

SORBENT FIBER PROPERTIES

C -0.0117, average usable absorber capacity per cycle, #SO_2/# absorber/cycle

L - .60, fiber loading, # absorber/# sorbent fiber

C x L - .007, #SO_2/#fiber/cycle

C is a function of the temperature and of the ambient SO_2 concentration. These values are for 200°F absorption from a simulated flue gas.

Non-thermally-desorbable (NTD) material accumulates in the fiber at the rate of approximately 1 percent of the SO_2 absorbed, leading to a gradual decrease in capacity and a need for periodic "decontamination" with a caustic rinse.

* * * * * * * * * * * *

As our sorbent will also react with SO_3, we expect the acid dew point to be depressed to the point that will permit discharge of de-polluted flue gas at a temperature of 200°F*. If we absorb at 200°F and regenerate at 260°F the sorption capacity will be reduced below that available with a lower sorption temperature, but we reduce the temperature swing of the process and avoid reheating the flue gas.

* Note that all temperatures in this Section and in Tables and Figures pertaining thereto are in °F.

The following assumptions are made about process operations:

1. Input flue gas from precipitator: 2,000,000 SCFM Composition I at 300°F and -19 [illegible] pressure.
2. Gas cooled to 200°F before contacting absorber.
3. Absorption of SO_2 and SO_3 occurs on contacting gas and precooled sorbent fiber, the heat of absorption heating the fiber from 190°F to 200°F.
4. Gas @ 200°F discharged to draft system augmented for pressure drop through cooler and absorber.
5. The sorbent fiber is regenerated by heating to 260°F and the SO_2 removed at high concentration.
6. The SO_2 leaves the process as a feed stream for reclaim.
7. The sorbent fiber is cooled to 190°F prior to its return to the absorption chamber.
8. After x cycles, sorbent fiber must be decontaminated of sulfates which reduce SO_2 capacity.

We visualize this process as being carried out on a continuous basis, with the sorbent fiber arranged in the form of a wide (or multiple narrow) continuous belt which passes at uniform speed from one unit process to the next. The quantity of belt in each unit is proportioned to the time necessary for completion of that unit function.

This approach is shown in Figure 27 in which the number labels correspond to the statements enumerated above. Not shown in the figure is the main belt drive, which would be applied to the regenerator, and fly ash collection equipment at the base of the regenerator. This figure is highly schematic, and is meant only to suggest relative size and possible means for carrying out the necessary steps. Direct permeation of the belt is shown in the absorption step. This might be impractical at a workable value of belt density, but it would reduce the exposure time to the minimum demanded by the diffusion of SO_2 into the fibers. Heating of the belt by steam heated "dry cans" is shown in the regenerator; since this is a closed box arrangement, the SO_2 would be emitted in relatively pure form. However, to prevent entrainment of SO_2 in the outgoing belt, and to remove ash, a steam purge of the belt before exit might be needed. This would cause dilution of SO_2 by steam which could be separated by condensation. In the belt cooler, cross-flow direct air cooling is shown; this would avoid the need to transfer heat through intervening materials.

The tank for decontamination of the belt with an alkaline solution, shown at 8, is shown in recognition of this need although a process has not been selected for this. In simulated flue gas about 1% of the SO_2 absorbed by the fiber becomes a sulfate contaminant and stays with the belt, reducing the absorptive capacity. For a period of time

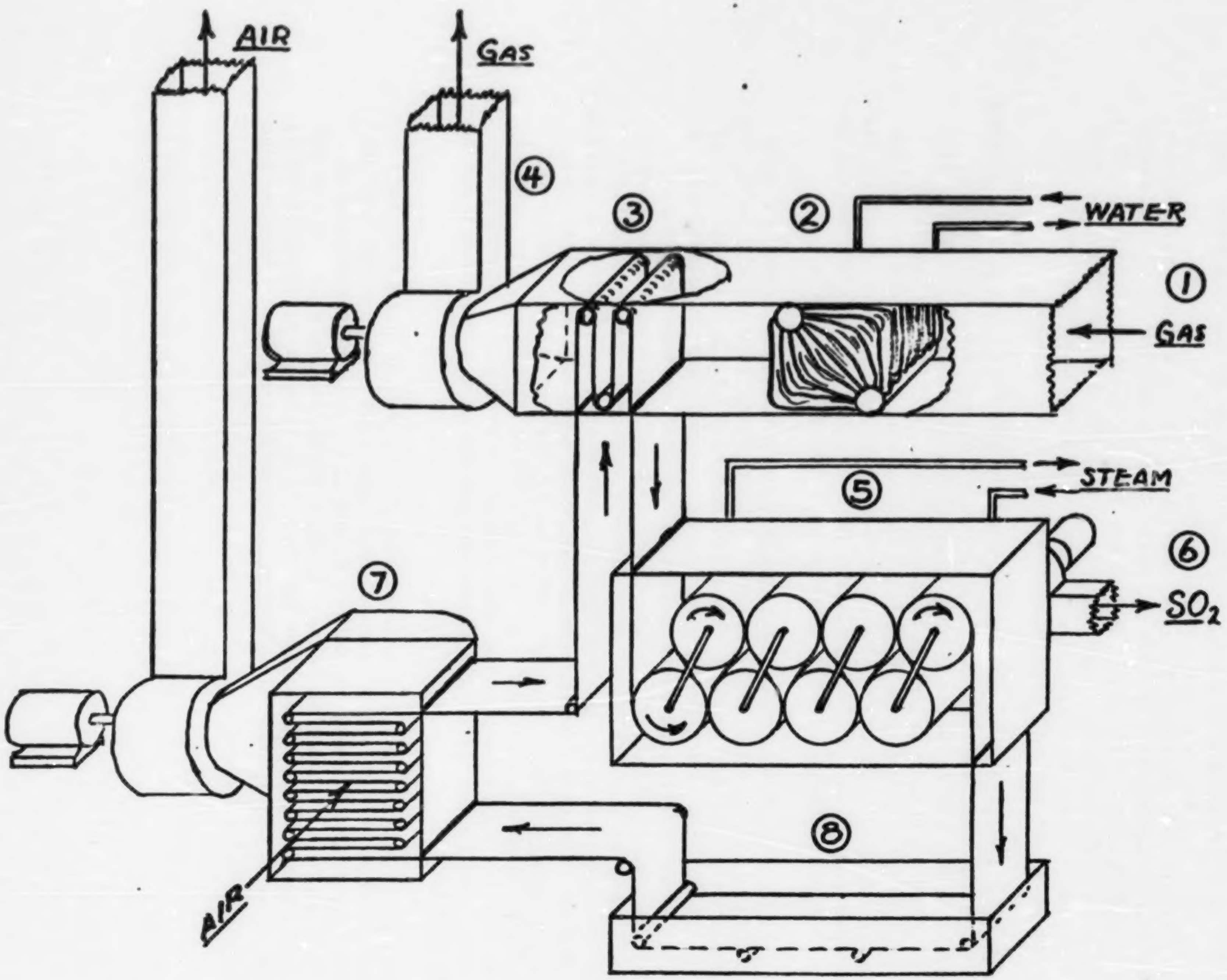

AIR
GAS
④
③
②
WATER
①
GAS
⑤
STEAM
⑥
SO_2
⑦
⑧
AIR

Fig. 27- Tentative Sorption Process

6/4/69
AB

which must be determined from the economics of providing overcapacity and from a knowledge of decontamination rate we do not now have, the belt must be immersed in a caustic solution to dissolve out the sulfate and restore the sorptive capacity for SO_2. In an actual installation, perhaps an additional 5% loss in capacity will be due to SO_3 present in the flue gas. This will hasten the need for decontamination. This may be avoidable by treating the gas with a particulate absorber such as ground limestone, which would then be removed with the ash by the steam purge at the regenerator exit.

In Figure 28 we see the amounts of primary materials per minute passing through the process, and the heat input or output of the different units. 9250 gpm of water @ 55°, discharged at 105°, in a 3000 square foot heat exchanger would cool the flue gas to 200°. Steam, in an amount determined by heating method and by the amount used for flushing belt and SO_2 dilution, would provide heat to the "dry cans" in the regenerator. 2.12×10^6 SCFM air @ 80°, discharged at 170°, acting on a 1/4 minute charge of belt, should cool the belt to 190°.

An actual determination of belt quantity requirements cannot be made at this time, as they will depend on the heating rate of the belt, its permeability to gas or air, the diffusion rate of SO_2 into and out of the fibers, the woven density of the belt, and their interactions. A belt weighing 1 lb. per square foot would need an exposure rate of 145,000 square feet per minute. A belt speed of 20 miles per hour would require a width of 83 feet of belt. This could be subdivided to provide each stack with a plurality of active belts while a necessary complement of belts undergoing decontamination would be added. For purposes of a rough economic analysis, we have assumed a charge of sorbent material equivalent to two minutes of operation. To achieve this will require very rapid heat transfer, absorption and regeneration; further study of all these are needed to determine what can be accomplished.

Using the process and the assumptions above, we can arrive at some very tentative figures on direct operating cost elements and capital cost elements as shown in Tables XL and XLI. The uncertainties in their derivation must be borne in mind; these can only be removed by experimental work, under high rate and long term conditions, which is specifically directed to diffusion, absorption and heat transfer rate measurements.

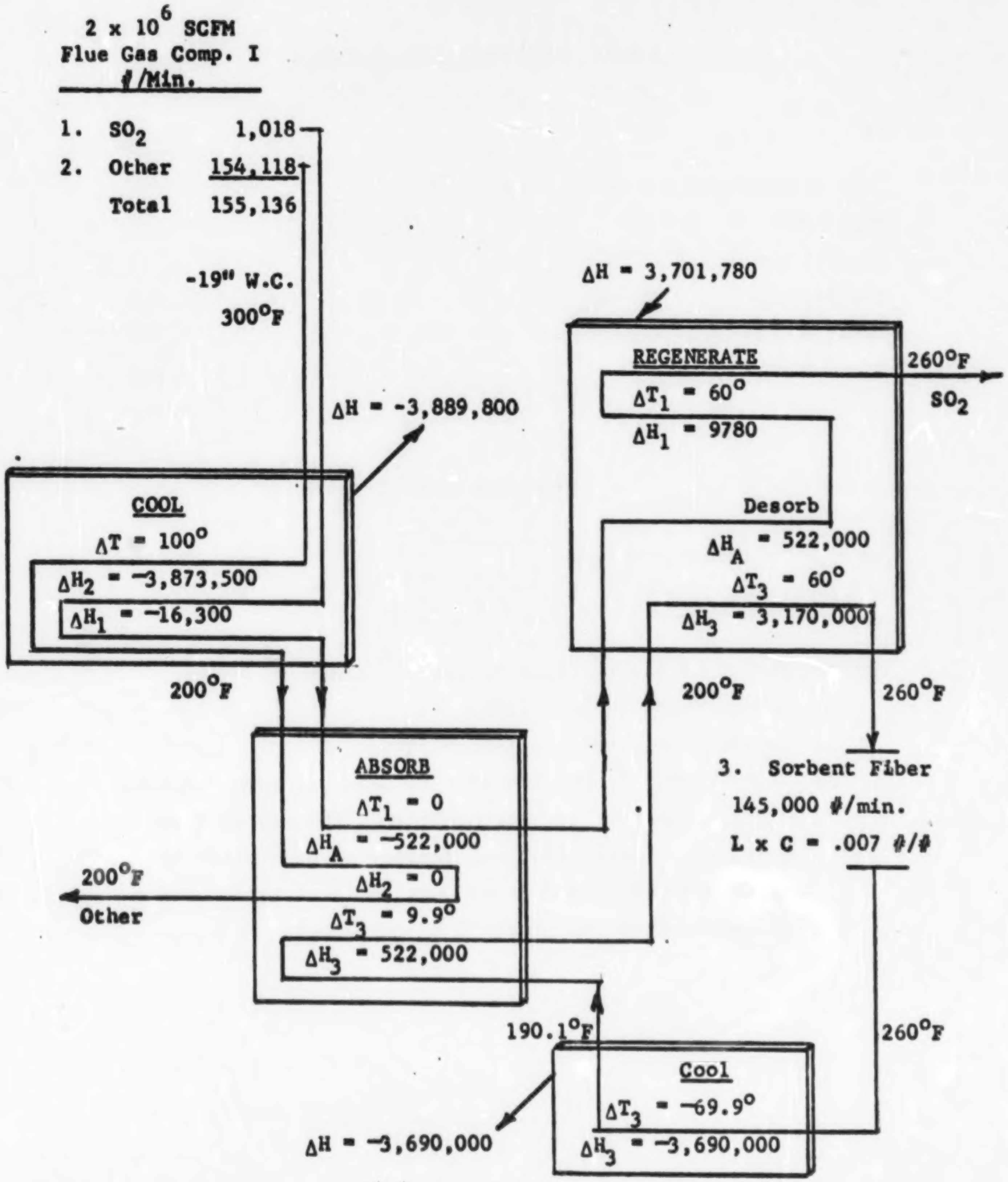

2 x 10^6 SCFM
Flue Gas Comp. I
#/Min.
1. SO2 1,018
2. Other 154,118
Total 155,136
-19" W.C.
300°F
ΔH = -3,889,800
COOL
ΔT = 100°
ΔH2 = -3,873,500
ΔH1 = -16,300
200°F
ABSORB
ΔT1 = 0
ΔHA = -522,000
ΔH2 = 0
ΔT3 = 9.9°
ΔH3 = 522,000
200°F
Other
ΔH = 3,701,780
REGENERATE
ΔT1 = 60°
ΔH1 = 9780
Desorb
ΔHA = 522,000
ΔT3 = 60°
ΔH3 = 3,170,000
260°F
SO2
200°F
260°F
3. Sorbent Fiber
145,000 #/min.
L x C = .007 #/#
190.1°F
260°F
Cool
ΔT3 = -69.9°
ΔH3 = -3,690,000
ΔH = -3,690,000

Fig. 28 - Material and heat balance (ΔH in BTU/min., fly ash ignored)

Table XL

DIRECT OPERATING COST ELEMENTS

(Labor & Supervision Excluded)

	$/min.
Belt Replacement - 6 month life	1.220
NH_3 - 26#/min. @ 5¢/#	1.300
Draft Augmentation 6" wc	.316
Cooling Air 4" wc	.210
Water @ 10¢/1000 gal.	.925
Steam @ 50¢/10^6 BTU	1.850
	5.821

OPERATING CREDIT

SO_2 1018#/min. @ 3¢/#	30.540

Obvious points of attack on operating costs are

1. Improvements in belt life.
2. Reduction of contamination effect.
3. Improvement of heat transfer to belt and some recovery of flue gas heat for regeneration. Changes in fiber contours or texturization, density of belt weave or knit, and use of fluidized beds for heat transfer are all approaches which should be evaluated.

Table XLI

CAPITAL COST ELEMENTS

Major Items of Equipment

Sorbent Belt - 290,000# initial charge	$ 290,000
Regenerator	500,000
Belt Cooler	300,000
Draft Augmentation - 6" wc	300,000
Cooling Air - 4" wc	200,000
Heat Exchanger	33,000
Motors, Controls, Pumps, Wiring	30,000
	$1,653,000

These figures represent a significant fraction of the items required for this process. The belt estimate depends on carrying out the cyclic process in 2 minutes, which could be overly optimistic.

Regenerator and Belt Cooler estimates are also very rough guesses.

At a Lang's factor of 4, the fixed capital requirement becomes ca. $6,600,000.

We are not in a position, at this stage of investigation, to make other than very tentative forecasts of the economic or the engineering features of a full size installation using fiber absorption of SO_2. More accurate economic forecasts depend on a more concrete mechanical and process layout, which in turn will require further study of process variables in the range of conditions to be met at operating scale. To summarize the engineering and economic position, we review here some of the unknown or inadequately known factors that will enter into, and must be determined for, a full scale design:

Fiber Properties: Effect on SO_2 capacity of temperature, gas velocity and state of contamination by sulphates. Saturation, regeneration and desulphation times under high rate conditions. A beginning has been made on these, suggesting a loss of capacity at high space velocities.

Belt Properties: Weave construction for high density fabric which is still open enough for reasonable permeability. Heating rates attainable with different heating methods. Speed, width, thickness for space requirements. Strength, power to drive, and tolerable bend radius for mechanical layout with suitable space and life characteristics. Cost.

Input Flue Gas: Range of temperature fluctuations with power plant load. Absorption should take place at a constant temperature high enough to give buoyancy but low enough to give adequate SO_2 absorption.

Effluent Flue Gas: State of de-pollution and exit temperature subject to specification. Augmentation of draft to overcome pressure drops in cooler and absorber.

Effluent SO_2: Temperature, pressure and state of dilution desirable for reclaim process input must be coordinated with that desirable for regeneration and for flushing SO_2 and ash from the belt. Regeneration is not likely to be effective in a 100% SO_2 atmosphere. Exhaust fan and/or condenser. Byproduct credit.

Flue Gas Cooling: Conventional -- controlled. Mechanical layout and space requirements. Area. Pressure drop. Possible thermal pollution of cooling water. Cost.

SO_2 Absorption: Belt charge as influenced by residence time of gas in belt and of belt in gas. Mechanical layout and space requirement. Pressure drop including effect of ash and alternate SO_3-absorbing additives. Cost.

Regeneration: Belt charge as influenced by residence time for transfer of heat to fibers and diffusion of SO_2 from fibers. Dilution of SO_2 for flushing. Ash removal and handling. Mechanical layout and space requirement. Cost.

Belt Cooling: Belt charge as influenced by residence time for heat transfer. Heat transfer coefficient. Cooling air conditions, pressure drop and fan capacity. Mechanical layout and space requirement. Cost.

NTD Removal: Belt cycles to exhaust SO_2 capacity -- with and without alternate SO_3-absorbing additive to be removed with ash. Desulphation method to be used. Belt charge as influenced by residence time, total treatment time per belt and belt treatment speed. Handling of desulphation chemicals and disposal of spent waste. Mechanical layout and space requirement. Cost.

6.0 CONCLUSIONS

1. Polymers containing tertiary aliphatic amino groups are efficient, regenerable sorbents for SO_2. A styrene-dimethylpropylmaleimide copolymer (SSQ) which contains tertiary aliphatic amino groups pendant from the polymer backbone is the sorbent of choice because of its exceptional resistance to degradation by flue gas components.

2. Polypropylene is a preferred fiber-forming constituent because it is unreactive and is easily spinnable. It is possible to prepare polypropylene fibers with acceptable physical properties containing as much as 60% SSQ.

3. The sorption capacity of polypropylene-SSQ fiber diminishes rapidly with increasing temperature. This is useful for thermal regeneration purposes, but places a limit on the temperature which can be used for sorption (probably about 95°C for this system). SO_2 sorbed by the fiber can be readily desorbed thermally by treatment with a sweep gas, steam or vacuum at 125-150°C.

4. The presence of water vapor in the gas stream gives a significant increase in SO_2 sorption capacity. The amount of water vapor normally occurring in flue gas is sufficient to reach the range of maximum sorption.

5. With simulated flue gases, an accumulation of non-thermally desorbable (NTD) material occurs which reduces the regenerable SO_2 capacity of the fiber with succeeding cycles of sorption and regeneration. This NTD material has been identified as sulfate, and is formed by the oxidation of SO_2 by oxides of nitrogen and/or oxygen present in the simulated flue gas. Treatment of the fiber with aqueous base at $pH > 9$ removes essentially all of the sulfate, and restores the sorptive capacity of the fiber.

6. The process in its current state shows promise for controlling SO_2 emissions from cooler effluents, particularly those having compositions which do not favor the oxidation of SO_2 to sulfate.

7. The two chief areas where further improvement is indicated for use in power plant emission control are (a) increasing the SO_2 capacity of the sorbent at high temperatures and (b) preventing or reducing the formation of NTD material.

7.0 RECOMMENDATIONS

Further work on this project should give high priorities to minimizing absorption and regeneration times under actual conditions, to developing rapid NTD removal procedures, to construction of actual belt samples for determination of thermal and mechanical properties, and to developing a bench-scale pilot plant to permit study of the variables and their interactions on a cyclic basis for large numbers of cycles.

In addition, further work in materials research should be carried out to develop amine-containing sorbent polymers which can function as sorbents at higher temperatures.

8.0 REFERENCES

1. "Development of Regenerable Fibers for Removal of Sulfur Dioxide from Waste Gases: Technical Report covering the period January 1 to June 30, 1968." Ronald W. Fuest and Merlin P. Harvey, report dated November, 1968. Obtainable from Clearinghouse under PB No. 185-093.

2. A high molecular weight polyethylene oxide produced by the Union Carbide Corp.